REQ. NO. 1-9032

CONTRACT REPORT NO. OSU81-00087

SHORT RESIDENCE TIME PYROLYSIS OF COAL

FINAL REPORT

by

Donald S. Scott
Principal Investigator
Department of Chemical Engineering
University of Waterloo

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology (CANMET); Energy, Mines and Resources, Canada.

DSS File No: 20SU.23440-1-9032
DSS Contract Serial No: OSU.81-00087
CANMET Scientific Authority: Dr. James F. Kelly,
Dr. S. Fouda

Contract Manager: Waterloo Centre for Process Development,
University of Waterloo,
Waterloo, Ontario.

MICROMEDIA
OCT 27 1982

72pp.

Short Residence Time Atmospheric Pressure Pyrolysis of Coal

Final Report

Donald S. Scott, Dept. of Chemical Engineering, University of Waterloo

DSS Contract 20SU, 23440-1-9032

CANMET Serial No OSU 81-00087

1. OBJECTIVES OF THE PROGRAM

This program was initiated on June 10th, 1981, with a termination date of March 31st, 1982 (later extended to June 1st, 1982). This report covers the activities during approximately eleven months of this period.

The objectives of the study set out three areas of activity;

1. To update the state-of-the-art review of flash pyrolysis and hydropyrolysis research contained in a final contract report submitted in July, 1980, by D. S. Scott (1).

2. To maintain contact with, and to report on experimental coal pyrolysis studies being carried out in Canada, especially those largely funded by CANMET.

3. To evaluate the behaviour of a Canadian coal during atmospheric pressure flash pyrolysis in a bench scale fluidized bed reactor.

All of the above objectives have been completed to the degree that was possible during the contract period, and have been exceeded in the case of the third objective. In particular, the degree of progress made by other experimental pyrolysis projects in Canada was not nearly so great as expected, with the result that the second objective was

not as significant a part of the contract study as had originally been expected. In addition, the severe cut-back for the funding of coal conversion research in the United States meant that much of this activity was at a lower level than in previous years. On the other hand, economic analyses reported during 1981/82 comparing coal conversion process costs have cast a more favourable light on pyrolysis methods, and so this approach has gained more credibility and attracted more industrial interest in both the United States and Canada. Rather than evaluating only one coal in the bench scale apparatus, three coals were studied, two Alberta sub-bituminous coals and one Eastern Canadian bituminous caking coal.

2. Assessment of the State-of-the-Art of Pyrolysis Processes - An Update from March 1981

This review covers only additional visits to research laboratories in North America since June, 1981. For a review of research prior to this date see the Final Contract Report for Contract OSU 79-00190 by D. S. Scott (1).

Visits were made to the following laboratories

(a) Brookhaven National Laboratories, Dept. of Energy and Environment, Long Island, N. Y. Dr. Meyer Steinberg; Head Process Sciences Division

(b) Institute of Gas Technology Chicago, Dr. Karl S. Vorres, Associate Director, Process Research Program Planning

(c) Cities Service Research and Development Co. Wayne A. Fling, Jr. Vice-President

Permission to visit Occidental Research Corporation in Los Angeles was refused by the Company, although a visit was made in 1980. In addition, discussions were held with Dr. J. Foong of the Alberta Research Council during his visit in August 1981 to the University of Waterloo, concerning the ARC flash hydropyrolysis program.

Summary of Work in North America

At the time of the visits in the fall of 1981, it is probably fair to say that most U. S. Laboratories were doing routine work on pyrolysis or hydropyrolysis, or else completing existing programs of tests. The reduced funding available from the Federal government has delayed many projects, at all levels. The impression

was gained that a careful and thorough re-assessment of coal conversion technology and economics was being carried out by many companies. Certainly, there was little evidence of new programs being actively planned or pursued. All laboratories were very anxious to carry out contract pyrolysis studies for external clients, presumably as an aid in keeping their research group and apparatus in functioning order.

(a) All of the laboratories visited have been involved heavily in the past in hydropyrolysis studies, primarily on a bench scale. At Brookhaven, experimental work on coal hydropyrolysis is being carried out on caking coals only. The high pressure reactor is in use for studies on biomass hydropyrolysis for a good part of the time. The tests with caking coals are being done using a coal - Cabosil mixture (10% - 15% by weight of Cabosil) to prevent agglomeration. Apparently this has been successful, although the effect of the Cabosil on the char ash content is still a question. According to Dr. Steinberg, work on coal is almost completed, inasmuch as they have accumulated "an adequate data base" which he sees as being their primary mission. The reactor tubing used was Inconel, which is not readily available. After about 1500 hours use, the reactor tube failed at 1000° C and 1000 psi.

Dr. Steinberg stated that he believed the U. S. Department of Energy now favoured a route to light hydrocarbon liquid through synthesis from CO and H_2.

(b) The Institute of Gas Technology has several experimental pyrolysis units. One has been described in publications and in earlier reports (1), that is, the 1/16 inch I. D. 200 foot long resistively heated coil type reactor. Feed rate is about 100 grams/hour in entrained flow, temperature 600°F - 1500°F and pressure to 2000 psig. Attempts were made to use this reactor for biomass, but with limited success, so it is now used for coal only.

At the pilot plant site a 3/4 inch I. D. 77 foot long coil type reactor is in use studying the hydropyrolysis of peat. Peat is fed at 5-10 lbs/hr., -16 + 100 mesh at temperatures of 1000° - 1500°F and pressures to 500 psig of H_2, or H_2 in other gas mixtures. Residence time is 4-10 seconds. Yields are about 40% char, and the highest liquid yield was 30% maximum as C_3 + for Finnish peat. Generally liquid yields are significantly lower for North American peats.

Another reactor at the pilot plant site is a coil type, 0.12 inches I. D., 70 feet of reactor section plus 20 feet of preheat section. This reactor is used to study lignite hydropyrolysis with 2-3 sec. residence time, 1300 - 1600°F, 2000 psi, being typical. Solids fed are -100 mesh, with 85% -200 mesh.

A "laminar flow" reactor under construction in 1980 at the time of the last visit in now in routine operation. It has a 2 inch I. D. reactor tube (enclosed in a pressure can) and operates to 1600°F and 1000 psig. The reaction zone can be varied from 6 inches to 8 feet in length. This reactor has been used to study the kinetics of devolatilization of caking coals (no problems were encountered since particles do not contact the walls until near the exit), and is now in use studying the pyrolysis of biomass particles. Feed rate is about 12 grams/hour. A report on "Rapid Rate Bituminous Coal Kinetics" is available from I. G. T. as a GIR Report. Coal devolatilization was measured at 1-2 sec. residence time and 800° - 1600°F.

The 'riser-cracker' concept for which a pilot unit was built and which has been described in the literature is not now being operated because of lack of both personnel and funds. At present, I.G.T. is planning to attempt commercialization of its peat hydropyrolysis process.

Inasmuch as I.G.T. is a commercial research organization, Dr. Vorres

would be very interested in testing Canadian coals.

(c) The Cities Service and Rockwell International hydropyrolysis developments are now run by a single group, with Dr. Fling as head of the CS/R management committee. The CS unit, located at the Tulsa Research Centre (formerly in New Jersey) is the one which has been described in numerous publications. It is a coil type hydropyrolysis reactor with interchangeable reactor coils having I.D.'s from 1/8" to 1/4". One reactor is a "laminar flow" type used for caking coals with a 3 inch I. D. Residence times obtained by the use of various reactors range from 0.5 to several seconds, temperature is normally 1500 °F, and pressure 500 - 1500 psig.

These hydropyrolysis reactors have been used to evaluate Alberta Forestburg coal (commissioned by SNC group, Montreal in 1980). Presently, tests are also being done for the Alberta Research Council on Wabamun coal, and tests on Sundance coal have been done also, according to Dr. Fling. These low volatile coals can yield up to 20% liquids, with 10% - 20% of this being BTX or similar light liquids. Gas yield is 12% - 16% and char 40% or more. The char is of the same physical nature as the coal fed, but it is less reactive.

While the CS and Rockwell approaches to hydropyrolysis are quite different (Rockwell uses rocket injection type mixers and reaction chambers with 50 - 100 ms. the optimal residence time), Dr. Fling says results from the two reactors correlate well where they overlap, although he stated wall effects were pronounced in the CS coil reactors.

In discussing the economics of the process, Dr. Fling sees the CS/R process as a "stand alone" operation, with char used for hydrogen manufacture.

He stated that the economices look favourable for commercialization, probably in the 1990's. Hydropyrolysis for maximum gasification is more economical that hydropyrolysis for maximum liquefaction. The liquefaction mode still yields too much gas and liquids with too low a H/C ratio. It was inferred that the lower the temperature the better the product quality.

Funds have apparently been received by CS/R to permit the Rockwell type reactor to be built at 0.25 to 1 ton/day feed rate in a continuous integrated unit. Funds received were apparently less than desired, so that the progress of this PDU seemed a little uncertain at present.

Hydropyrolysis results for Alberta coals and a conceptual design have recently been published by Cities Service (2) at the 2nd World Congress of Chemical Engineering, Montreal, October 6, 1981.

Dr. Fling said that CS was quite prepared to dedicate the Tulsa reactor to a client, and costs would be about $1500 per sample (presumably, per data point).

Additional details of the current work being carried out in these three laboratories may be found in a recent paper by Fouda (3).

Although a visit to Occidental Research Corporation could not be carried out, research is continuing using the ORC pyrolysis process employing the new 2 kg/hr "bench-scale" continuous unit described previously (1). Current studies have resulted in a so-called "Controlled Flash Pyrolysis" process which has recently been described by Che et al (18). Basically, the process is modified by using a reactive gas (CO_2 or H_2O) to nullify the deleterious effect of hot char on liquid yield, and by quenching pyrolysis vapours with a hydrogen donor solvent

(tetralin). Maximum liquid yields of about 25% (maf.) were obtained at 700°C and 1 sec. from a Wyoming sub-bituminous coal.

(d) There has also been a noticeable increase in literature articles emanating from U. S. laboratories during 1980-82 describing more fundamental studies on pyrolysis and hydropyrolysis. Many of these investigations of thermal pyrolysis are undertaken as a part of a program on gasification studies. No attempt will be made to give a complete summary of the literature - bibliographies and summaries are available elsewhere. (eg. - 19) However, there are some articles worth singling out because of the additional information on pyrolysis chemistry or kinetics they afford.

Of the several articles presenting kinetic evaluation of coal pyrolysis, two articles by Gavalas et al are useful (20) (21). A very comprehensive kinetic model for pyrolysis is presented, but in particular, a compilation of 42 elementary reactions in coal pyrolysis is given and kinetic parameters - pre exponential constants and activation energies - are given for 38 of these.

The effect of alkaline cations has been explored in several articles, both present in the indigenous mineral matter, (15) (16) (17),which is discussed later, or added for desulfurization (22).

A detailed study of the effect of pre-oxidation on the pyrolysis behaviour of caking coals has been presented by Maloney and Jenkins (23), who used a laminar flow type reactor. For short residence times e.g. from 0.1 to 0.3 seconds, pre-oxidation reduced liquid yields significantly. Char obtained was in the form of cenospheres.

An atmospheric pressure entrained flow reactor was fitted with <u>in situ</u>

infra red analysis, and species formed were measured at 800° - 1200°C by Solomon and Hamblem (24). It was found that the kinetics of gas formation were insensitive to coal rank. Olefins and acetylene were formed by cracking of parafins. Functional groups in coals were found to react in the order - aliphatics, the hydroxyls and carboxylic acids, followed by aromatic hydrogen and ether linkages.

Coal pyrolysis at high temperatures (to 1600°C) and pressures to 30 atm was reported by Tamhankar et al (25). Yields of volatiles increased steadily as temperature varied from 800°C to 1600°C in N_2, CO_2, or H_2O, and although trends varied somewhat, yields were similar. At very high temperatures (1400 C) yield of volatiles in N_2 - H_2O atmosphere decreased with pressure, whereas at lower temperature (800°C) the yield increased with pressure. At about 1000°C, pressure had little effect.

Summary of Work in Canadian and Other Laboratories

In June, 1980, a contract was awarded by CANMET to Kilborn Engineering Ltd. of Toronto to design, construct and operate a bench scale high pressure flash hydropyrolysis unit to have a feed rate of about 1 kg/hr. The unit is patterned to a considerable degree on the design developed at Brookhaven National Laboratories and has been described by Fouda (3). At the present time (April, 1982) the unit has been designed and constructed, and start-up should take place in 1982. It is hoped to develop fundamental information for the processing of Canadian coals by flash hydropyrolysis.

Concurrently with the above work by Kilborn, the Alberta Research Council had also designed and constructed in Edmonton a high pressure flash hydropyrolysis unit, patterned largely after the Cities Service helical coil type. As of

April, 1982, this unit had not yet been fully assembled. With the recent departure of the project leader, Dr. John Foong, from the Alberta Research Council, the present status of this work is uncertain.

More fundamental studies are proceeding in several Canadian laboratories. Stangeby and Sears (8) reported additional results on pyrolysis of several Canadian bituminous coals using the MIT pyroprobe type of apparatus at both atmospheric pressure and under hydrogen pressure. Results generally confirmed those reported in earlier work, with liquid yields up to 10% (carbon conversions) being obtained at optimum conditions.

Furimsky, Belanger and Jorgensen reported on correlations of Fischer assay volatiles and liquids with H/C ratios or mean reflectance for thirteen Canadian coals (13). Lower rank coals did not correlate as well with H/C ratio, but gave yields of hydrocarbon liquids lower than was expected. For this reason, it was concluded that these coals were less suitable for pyrolysis, and that this type of test could be used to assess the pyrolysis performance of coals. However, since the hydrocarbon yield from lower rank coals can vary from 90% to 180% of the Fischer assay value (7) it is apparent that the method of pyrolysis is also a factor which must be taken into account.

Bench scale pyrolysis studies continue at the University of Waterloo as reported by Scott(9), utilizing an atmospheric pressure bench scale fluidized bed with a vapour residence time of about 0.44 sec. Maximum liquid hydrocarbon yields were obtained at about 650-700°C, in agreement with other reported work (14). Two Alberta sub-bituminous coals by analysis gave about 11-11.5% liquid hydrocarbon yield (maf) (about 15% carbon conversion basis). At 750°C, the hydrocarbon liquid yield from these coals fell to about 9% maf, but the BTX rose from about 3% of the liquids at 650°C to about 15% at 750°C. Total volatiles increased

steadily with temperature. The above results have not been normalized to 100% carbon balance, as is normally done in other reports. When the bench scale results are used so that liquid hydrocarbon yield is determined by difference, as is commonly done by other workers, then yields maf basis become higher. A 2kg/hr pilot plant is now under construction, designed for the flash pyrolysis of both biomass and coal in a fluidized bed.

Work on the pyrolysis of high volatile bituminous coal under vacuum is also underway by E. Chornet at the University of Sherbrooke. At the time of preparing this summary we had been unable to obtain any reports, although at least one internal report has apparently been prepared. Because the Energy Research Laboratories of CANMET are in the best position to be aware of government funded programs on coal conversion in Canada, whether these are federally or provincially supported, and of the existence of final program or contract reports, it would be useful if CANMET could supply listings of titles of such non-public documents to other workers in the area. Even a modest quarterly listing mailed to CANMET contractors and grantees would be a useful beginning.

Additional Australian studies reported by Smith (14) have shown that if lower rank brown coals and sub-bituminous coals, which have a significant oxygen content are pre-treated with HCℓ that tar yields are significantly improved, by up to 50%. The tar yield vs. H/C ratio correlation for the low rank treated coals agrees more closely with that for bituminous coal than do the values obtained from untreated coals (cf. Furimsky et al (13)). This improvement in yield is due to the fact that up to one third of the oxygen in lignites or similar coals is present in carboxylic acid groups, which can act as cation exchangers with sodium, potassium, calcium or magnesium. These cations are known to decrease liquid hydrocarbon yields in pyrolysis (e.g. Franklin et al, (15) (16), Tyler and Schafer (17)). By exchanging these with hydrogen by acid treatment, tar yields are increased very significantly, to a level commensurate with the H/C ratio of the coal.

Commercial Development

The Utah Power and Light Co. recently declared its intention to proceed with the development of an integrated atmospheric pressure thermal pyrolysis plant and an electricity generating power station (4) (5). A washed Utah high volatile bituminous coal will be used a a rate of 20000 TPD in the commercial plant, to yield about 21,000 bbls/day of synthetic (upgraded) crude oil and 1650 MW of electricity from char. In practice, UP&L plans to burn a 40-50% char-coal mixture in order to minimize operating difficulties. A 1000 TPD demonstration plant would first be constructed after pilot plant tests at 10-25 TPD to yield engineering data. Commercial scale operation is planned for 1988-89. No decision on the pyrolysis process to be used has been made as of March, 1982, but either the Toscoal (6) or Lurgi-Ruhrgas (7) process apparently will be selected. Both Utah Power and Light (5) and Toscoal (6) have presented economic analyses of the proposed project. Some details given in these recent reports may be of interest.

Roughly 1000 bbls of upgraded crude result from every 100 MW power generated. Based on the incremental coal required because of the pyrolysis process, oil yields are about 3 bbls/ton of coal.

Excluding coal cost, direct operating costs are $7.43/bbl (Toscoal)

With no credit for char produced, capital cost of an atmospheric pressure pyrolysis plant is $30,000 per bbl per day of syncrude capacity, of which the upgrading facility (hydrotreating) represents 60-70%. (UP&L)

It is cheaper to hydrogenate pyrolysis oils downstream than to directly hydrogenate coal. Low conversion pyrolysis processes are much cheaper than direct or indirect liquifaction. (Lurgi)

High overall thermal efficiencies are possible if pyrolysis char and gas

can be used hot in a power generating unit.(Lurgi)

While char burns more slowly than coal, it can be used in existing boilers. The upgrading of the pyrolysis oils is technically fairly easy (UP&L).

Char in storage is not pyrophoric, and could be stored if essential. (UP&L) A utility with coal pyrolysis could offset rising coal costs and reduce power costs.(Toscoal)

Both the Toscoal and Lurgi process use kiln type reactors, the former with hot ceramic balls as heat carrier, the latter with hot char. The Toscoal process cannot handle caking coals without pre-treatment, whereas the Lurgi process can. Both processes have successfully operated 25 ton/day pilot plants on Utah coals. The Toscoal process is based on oil shale retorting technology, which was to be proven commercially in the Colony oil shale project. With the recent cancellation of this development, the Toscoal process has suffered a set-back. On the other hand, Lurgi has experience with a number of pilot scale and demonstration scale pyrolysis installations in Europe.

It is interesting to observe that, despite the lack of interest in U. S. programs in atmospheric flash pyrolysis, this process is likely to be among the first to be commercialized in the United States as a source of hydrocarbon liquids from coal. This is likely to be the case also in Europe and Australia.

No similar large scale development for flash hydropyrolysis seems to be planned. Only the CS/R hydropyrolysis unit appears to be active at the PDU stage.

In Canada, the first workshop on the commercial potential of pyrolysis for Eastern Canadian coals was organized by the Atlantic Research Laboratory of

NRC in January, 1982. A number of papers presented there reflected a growing Canadian interest in pyrolysis processes. In particular, economic studies performed by SNC, Acres and Kilborn were presented and will be available in the Proceedings to be published shortly by the Atlantic Research Laboratory of NRC. An overview of work now underway in Canada on pyrolysis was given by Fouda (3). A summary of coal research, and development for Eastern Canadian coals is available in an ARL report also (11).

A series of technical studies on coal liquefaction processes for Canada has been undertaken by SNC under a contract with the Dept. of Energy, Mines and Resources (CANMET). Of the seven processes to be evaluated* one is the CS/R flash hydropyrolysis process. A detailed report in draft form is now available, which includes test results for Alberta Forestburg sub-bituminous coal. (12)

* Atmospheric flash pyrolysis is not one of the seven processes being studied in this contract.

PART II

Short Residence Time Pyrolysis of Coal

Experimental Results

Principal Investigator: D.S. Scott
Chemical Engineering Dept.,
University of Waterloo

WATERLOO CENTRE FOR PROCESS DEVELOPMENT

June 1, 1982

Short Residence Time Pyrolysis of Coal - Experimental Program

Introduction

The original work proposal (Contract No. OSU.81-00087) undertook to complete a series of tests on Alberta Forestburg sub-bituminous coal using the bench scale mini-fluidized bed reactor developed in an earlier contract (OSU.79-00190) and described in the final contract report (1). This apparatus, as well as the operating technique, were refined and put on a routine basis during a study of biomass pyrolysis completed in the period between the above two contracts.

In the current phase of the experimental investigations, which began on June 1, 1981, an additional 30 experiments on the Forestburg coal were proposed to study the effects of temperature, reaction atmosphere and particle size. Runs were completed on the Forestburg coal investigating temperature and the effects of reaction atmosphere. Additional analytical methods were developed during these tests to give better material balances and to allow an estimation of light hydrocarbon (BTX) produced to be made.

Because of the relatively low liquid yield from Forestburg coal - the primary objective of the fluid bed pyrolysis technique is to maximize liquid yields - and because of the interest in Alberta in another sub-bituminous coal from the Wabamun area (Highvale coal), a parallel series of tests were run with this coal. At the conclusion of these tests, following the workshop on pyrolysis of Eastern Canadian coals (Fredericton, N.B. January 1982) it was decided to attempt the pryolysis of the highly caking Devco Cape Breton coal in our bench scale unit. While these tests were successfully completed, after modification to the fluid bed reactor, there were still considerable experimental difficulties, and further tests should await the development (now underway in our laboratories) of a different design

for a bench scale reactor which is more suitable for the pyrolysis of highly caking coals, and which has a configuration amenable to scaling up.

In all, 39 pyrolysis runs were carried out. Reliable results were obtained for the sub-bituminous coals, and the mini-fluidized bed reactor was found to be entirely satisfactory for non-caking coals. Yields of organic liquids were about as expected and reported by others for similar coals, although there are problems in comparing bench scale pyrolysis results among various investigators, as is pointed out in later sections. BTX analysis is also available for these coals. However, carbon balances could only be estimated for two runs, because of the unreliability of C/H/N/S analyses contracted to a commercial laboratory. Our own apparatus for C/H/N/S analysis has been recently purchased and is now operational, and elemental analysis done in-house on the pyrolysis products will be a routine feature of future work.

Materials Used

Proximate and ultimate analyses of the three coals used are given in Tables 1, 2 and 3. Analyses given as from EMR (Dept. of Energy, Mines and Resources) or Alberta Research Council (ARC) are those supplied along with the coal sample. Analyses designated as "Guelph" were done by an independent laboratory on the coal sample used for pyrolysis tests. In the ultimate analyses of these coals, as well as in analyses of chars, the independent laboratory appeared to obtain low results whenever carbon was directly analyzed.

Table 4 shows the moisture and ash contents, determined for the samples of coal actually used in pyrolysis tests. These values were used in calculating the moisture, ash-free composition (maf).

Apparatus

The bench scale pyrolysis unit is shown in Figure 1. The details of the reactor used for non-caking coals are shown in Figure 2. These units are basically the same as those described earlier. Reaction conditions are summarized below:

Reactor: 316 stainless steel, net volume 26 mls.

Fluid Bed -60 +140 mesh Ottawa sand, 15 grams.

Vapour residence time 0.44 secs.

Temperature 450° - 800°C

Coal Feed Rate 15-30 grams/hour

Coal size -100 + 200 mesh.

The reactor as shown in Figure 2 was unsuitable for caking coals because of the tendency to coking and plugging at the point of injection of the coal particles into the fluid bed. Therefore, a modified gas-cooled injection tube was designed and used in the tests with caking coal. This modified injection tube is shown in Figure 3.

Table 1

Analysis of Alberta Highvale Sub-Bituminous Coal

Proximate Analysis (as received)

	ARC	Guelph
Moisture %	6.4	17.64
Ash	10.0	9.26
Volatile Matter	33.1	32.97
Fixed Carbon	50.5	40.13
Calorific Value	10364 BTU/lbs	

Ultimate Analysis

	ARC	Guelph
C %	75.4	70.82
H	4.1	4.35
N	1.0	2.90
S	0.2	0.11
O	19.3	21.82

Gray-King Assay (ARC)

Char %	68.8
Gas	15.0
Heavy Tar	4.8
Liquor	11.4

Table 2

Analysis of Alberta Forestburg Sub-Bituminous Coal

Proximate Analysis (moisture free)

	CS/R	EMR	Guelph
Ash %	5.6	7.79	7.41
Volatile Matter	42.0	45.90	46.52
Fixed Carbon	52.0	46.31	46.11

Ultimate Analysis

(dry, ash free)

	CS/R	Guelph	EMR
C %	73.3	62.12	72.48
H	4.5	5.03	4.54
N	1.3	1.31	1.53
S	.6	.11	.61
O	20.3	31.43	20.84
			11577 BTU/lb

Table 3

Analysis of Cape Breton Devco Bituminous Coal

Proximate Analysis (moisture free)

	EMR
Ash%	2.9
Volatile Matter	35.4
Fixed Carbon	61.7

Ultimate Analysis

C%	84.7
H	5.6
S	1.3
N	1.3
Ash	2.8
O (by dif.)	4.3

Table 4

Moisture and Ash Contents of Coal as Fed

	Moisture %	Ash %
Forestburg	10.02	7.48
Highvale	17.5	9.60
Devco	1.2	2.80

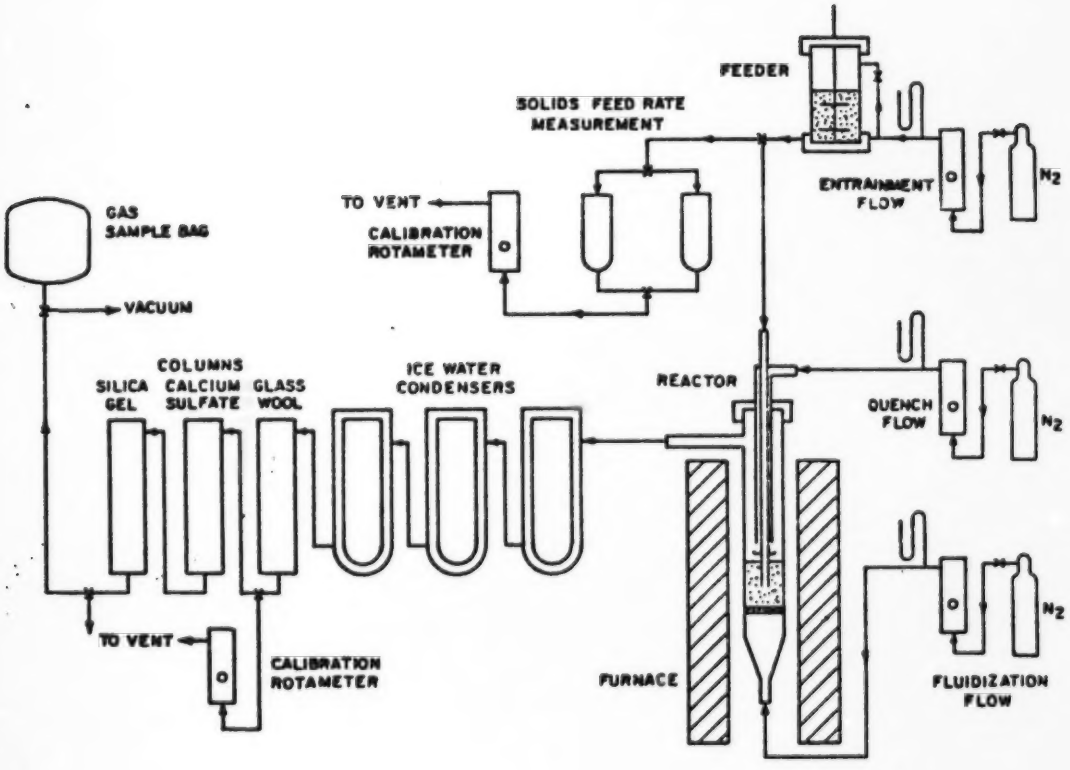


Figure 1 Fluid Bed Atmospheric Flash Pyrolysis Apparatus

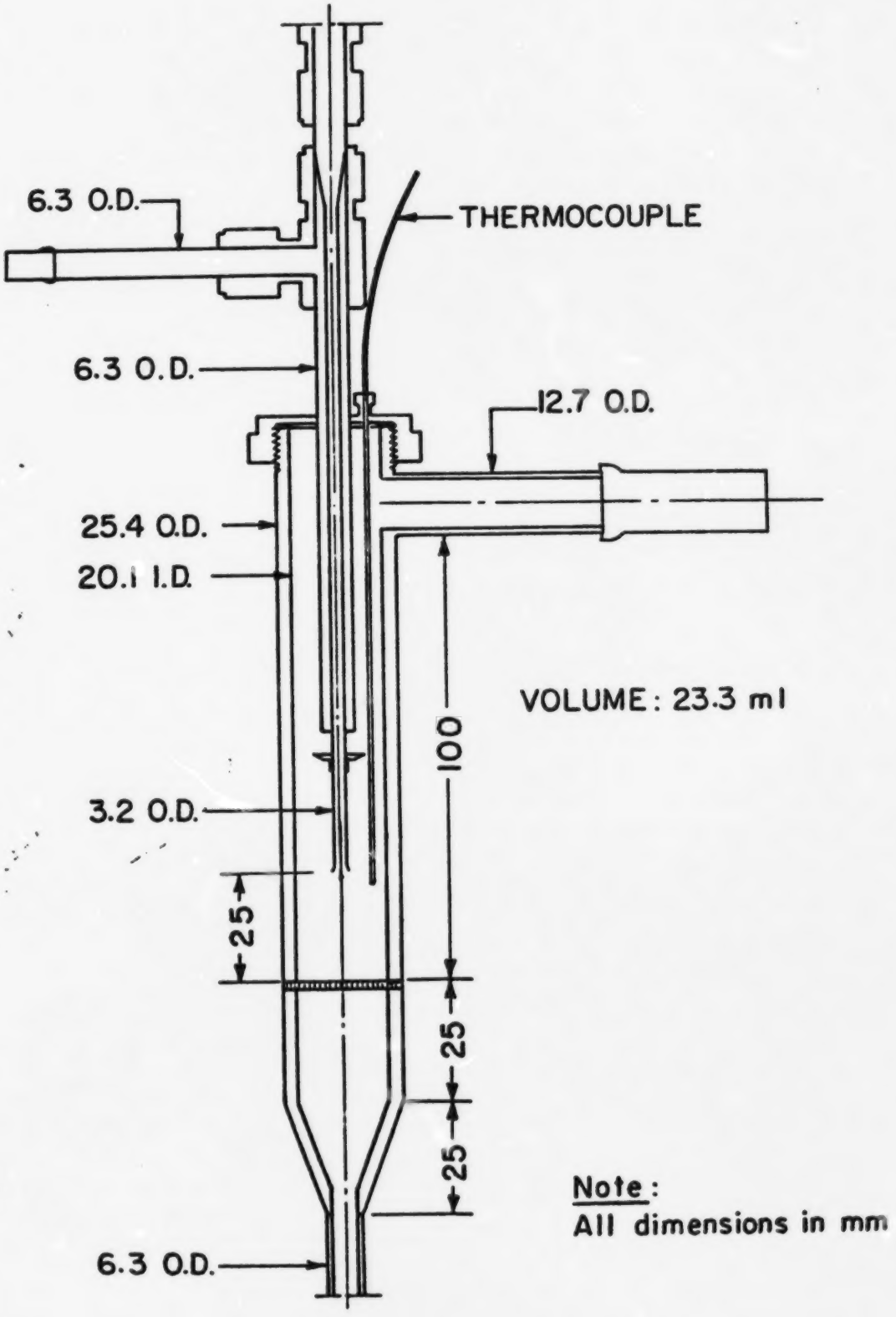
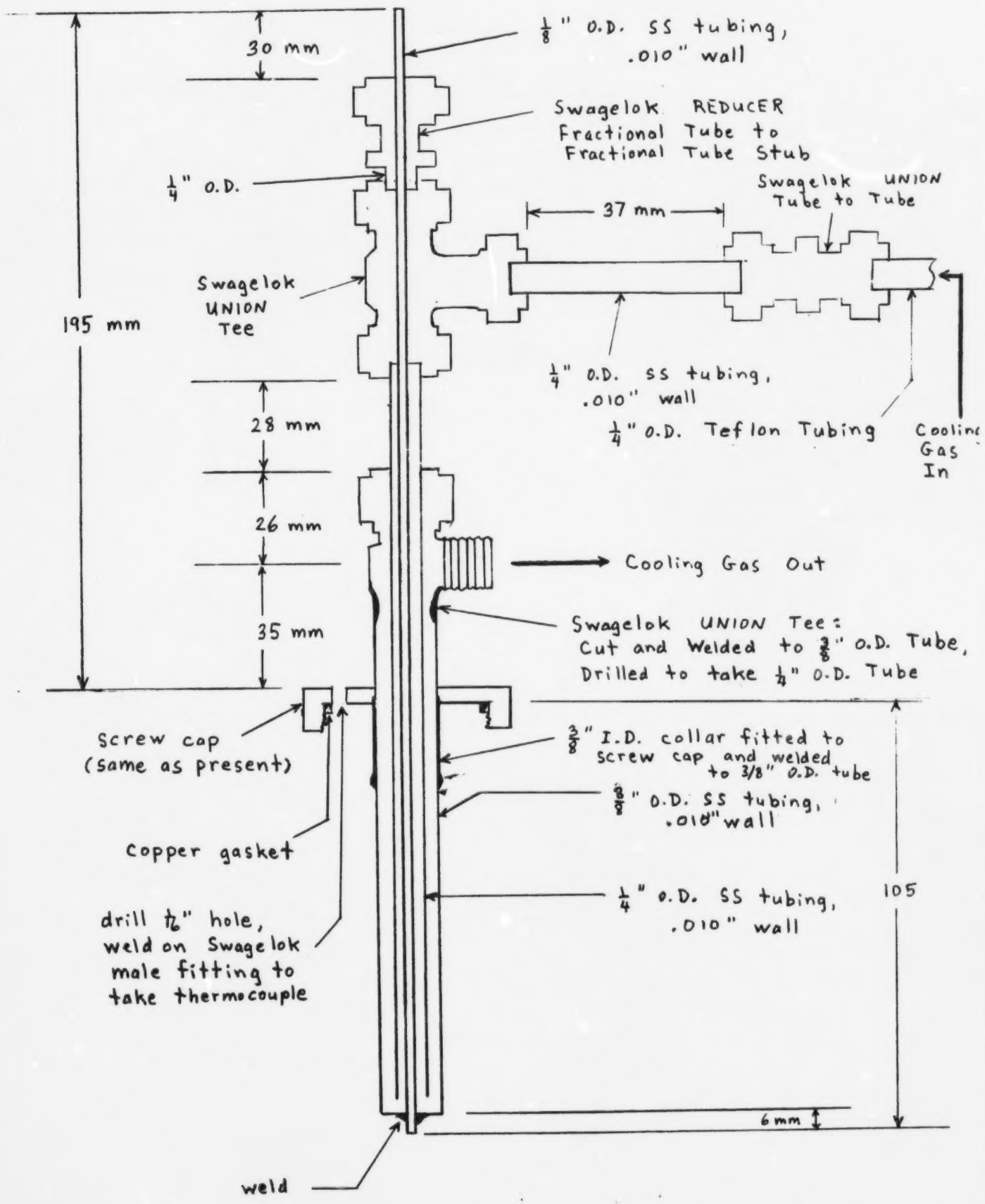


Figure 2 Diagram of Stainless Steel Reactor

Figure 3 Air-Cooled Coal Injection Tube for Caking Coals


30 mm
195 mm
28 mm
26 mm
35 mm
1/8" O.D. SS tubing, .010" wall
Swagelok REDUCER Fractional Tube to Fractional Tube Stub
1/4" O.D.
Swagelok UNION Tube to Tube
37 mm
Swagelok UNION Tee
1/4" O.D. SS tubing, .010" wall
1/4" O.D. Teflon Tubing
Cooling Gas In
Cooling Gas Out
Swagelok UNION Tee: Cut and Welded to 3/8" O.D. Tube, Drilled to take 1/4" O.D. Tube
Screw cap (same as present)
3/8" I.D. collar fitted to screw cap and welded to 3/8" O.D. tube
3/8" O.D. SS tubing, .010" wall
Copper gasket
1/4" O.D. SS tubing, .010" wall
105
drill 1/16" hole, weld on Swagelok male fitting to take thermocouple
6 mm
weld

Condensers were cooled by ice water. Gas samples for the analyzing of product vapour immediately above the fluid bed were taken through the quench gas line. Gas analysis of hot vapours was done by a Carle gas chromatograph sampling at 150°C. Because of the soot and heavy tars it was found necessary to install a filter ahead of the hot gas sample loop when pyrolysing coal. Analysis of the off-gases was done by dual column gas chromatography using a thermistor detector. Analysis of hydrocarbon gases and BTX was done using flame ionization detectors.

Procedure

The stainless steel reactor was first weighed empty, and then filled with exactly 15g of OTTAWA sand, sized -60 +100 mesh. The reactor was then placed in the oven and all inlet and outlet lines attached. The Scott feeder was weighed without the top (due to balance limitations) and then installed. A column of glass wool was weighed and the product collection system completed. A small flow of nitrogen was sent through the fluidized bed during heating. An ice water bath was prepared for two condensers. The gas sample bag was evacuated prior to the run.

For the caking coals, 20g of OTTAWA sand, size -30 +60 mesh were employed with the gas-cooled coal injection tube.

A run was begun by starting the appropriate gas streams and beginning stirring in the feeder at 250 RPM. During the run, hot gas samples were injected into a Carle GC to detect the water content of the product gases. A 1 ml sample was also injected into a Perkin-Elmer Sigma 3B GC equippped with an FID (flame ionization detector) and Fluorad column in order to detect BTX.

All run data were reported on a run data sheet. An example is shown in the Appendix, along with sample calculations. A run was generally

about 30 min. in length.

Analysis

Gas samples (1 ml) were injected from the gas sample bag into a Perkin-Elmer Sigma 4 GC equipped with a thermistor detector. Two columns, Molecular Sieve 5A and Chromosorb 102 allowed for separation of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene and ethane.

After cooling, the sand and char were removed from the reactor and weighed. All teflon lines, condensers, and the reactor were washed thoroughly with dichloromethane. The extract was then filtered through previously weighed filter paper. The filtered extract was evaporated to near dryness at 65°C. The remaining extract was placed under a vacuum at an absolute pressure of 400 mm Hg. for 1 min. The process was then repeated using acetone as the solvent.

The reactor was weighed, along with the glass wool column, and the Scott feeder. The filter paper used in the solvent extraction was placed in an oven at 110°C for 30 mins. and then weighed.

Many problems were encountered in early runs obtaining a complete material balance, with the total yield amounting to less than 90% of coal fed. The main problem was finally found to lie in the analysis of water content in the product gases. This difficulty was largely due to the soot and heavy tar in these gases, which could deactivate the GC column. In order to correct this problem, an easily repeated calibration was developed using air saturated with water vapour at 25°C. The calibration was repeated weekly to check on column activity.

BTX Calibration

The production of the benzene-toluene-xylene fraction could not be quantified in the usual manner of GC analysis as only a liquid calibration mixture was available. Because peak shapes obtained from injection of gas samples and liquid calibration samples were different, areas from a liquid

calibration standard and hot off-gases had to be compared. However, a suitable integrator was only obtained after run 24. Thus, the following procedure for BTX yields was developed for earlier runs.

1. Toluene was chosen as an external standard for all BTX compounds. Response factors were then determined for all BTX compounds by injecting equal amounts of each compound into the GC, and comparing the areas obtained to toluene.

2. Different amounts of toluene were then injected and the corresponding areas found to create an amount vs. area curve (toluene) and an adjusted area curve for other BTX compounds (Fig.4).

3. A height vs. adjusted area curve (Fig.5) was then developed using data for runs 25-29 for all BTX compounds. The adjusted area for a compound was the actual area multiplied by the inverse of the response factor.

The BTX yield could then be found using old chromatographs (those obtained prior to run 25) by reading the necessary peak heights and then finding the adjusted area using Fig. 5 . The amount for the 1 ml injection could then be found using the sum of the peak areas and Fig4 . Total BTX is then found by multiplying this 1 ml amount by the total volume of nitrogen and product gases.

This method contains several potential sources of error:

1. The run chromatographs were obtained from a single sample. However, the reaction itself will vary with time.

2. The older chromatographs may not follow the calibration, as column characteristics will change with time.

3. Errors are possible in the reading of the calibration graphs.

Still, the method appears to provide a good estimation of the BTX yield.

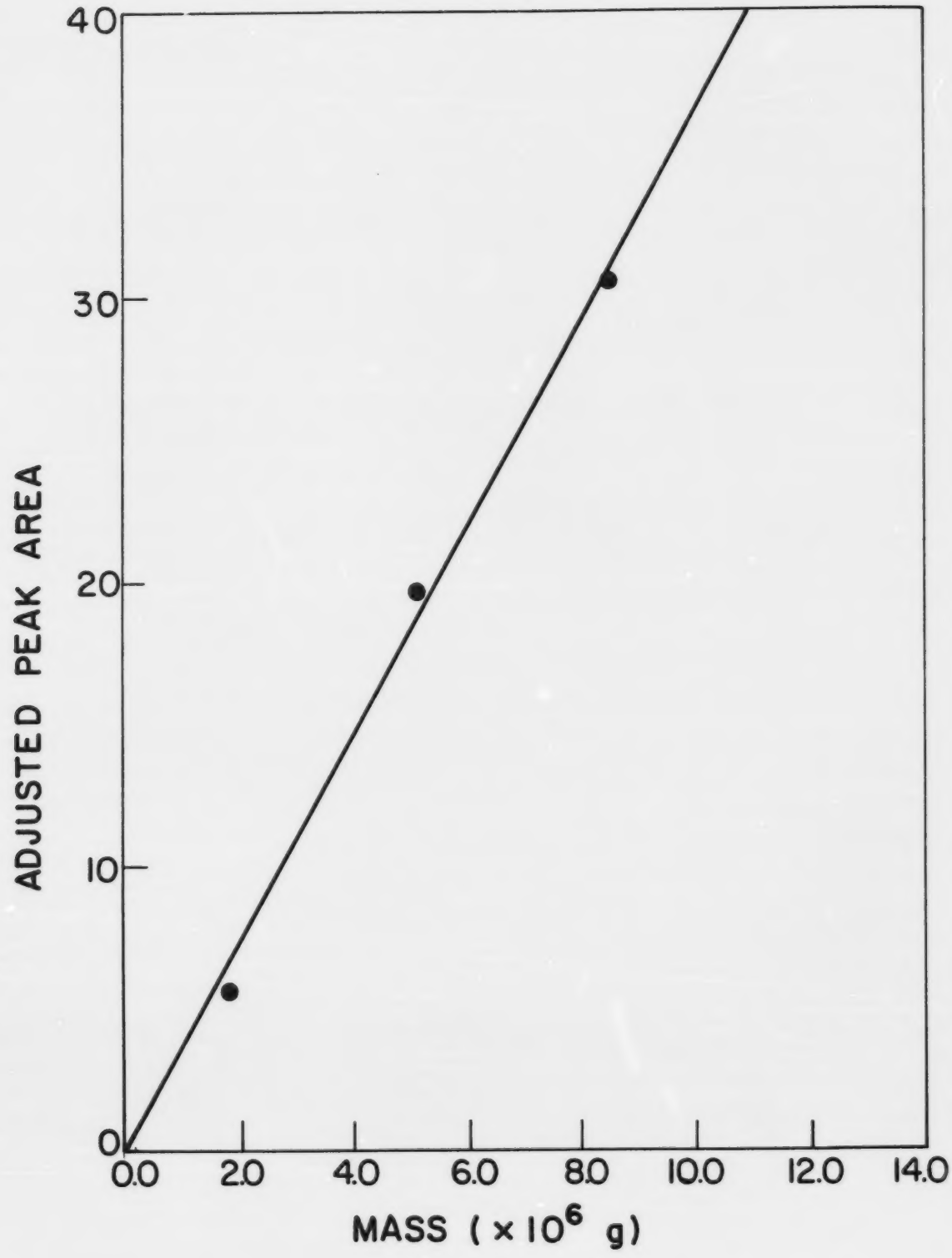


Figure 4 BTX Calibration - Adjusted Peak Area vs Mass

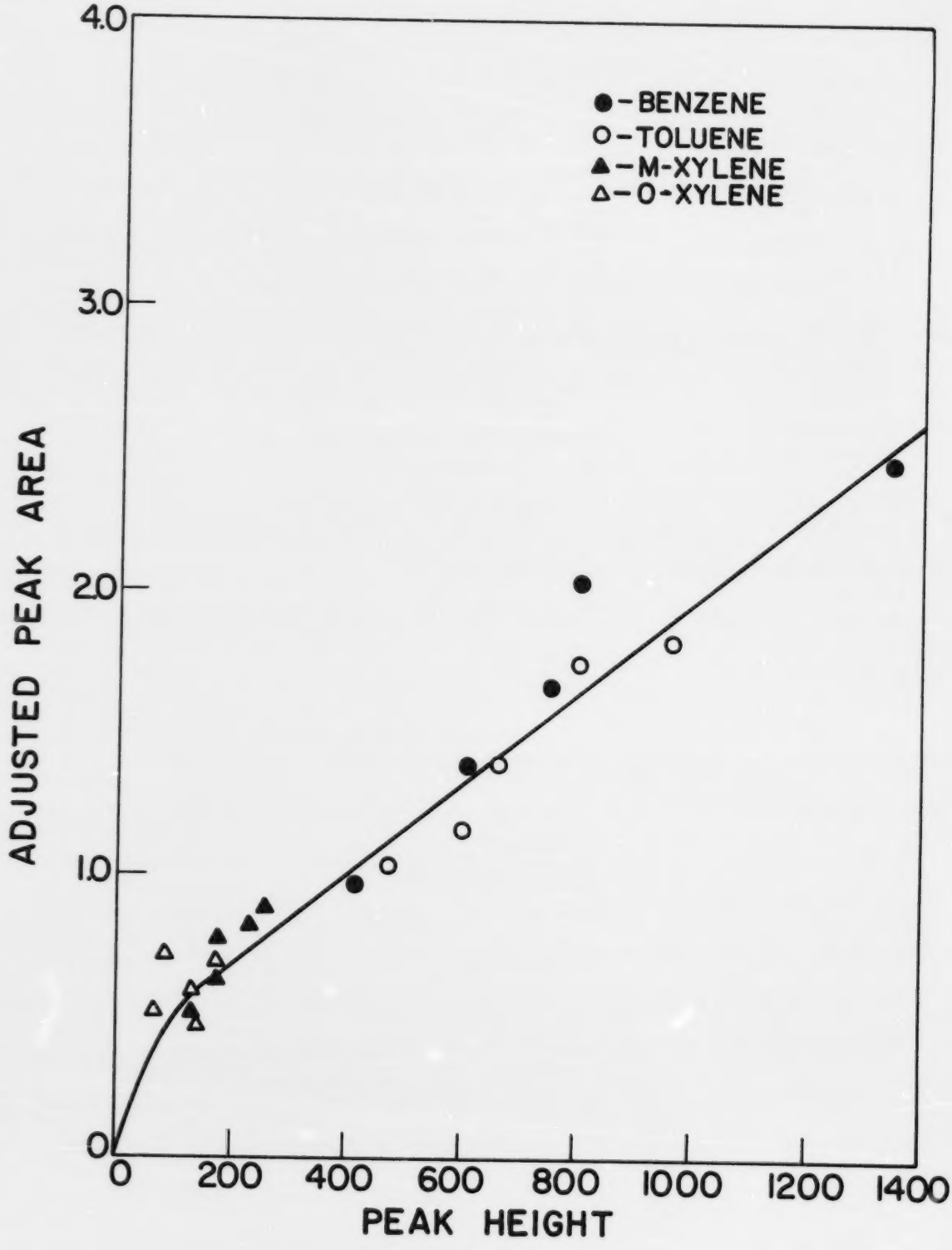


Figure 5 BTX Calibration - Adjusted Peak Area vs Peak Height

RESULTS

Forestburg Coal

The yields of volatiles and tar are presented in Fig.6 on a moisture and ash free basis. The product gas analyses are presented in Fig.7 and 8. Char yield is shown in Fig.9 and represents 50-65% of coal fed. None of the yields presented in these graphs have been normalized or adjusted for deficiencies in the material balance. Hence, our values appear somewhat lower, especially for tar, than those reported by others.

In general, it was found that total volatiles (tar + gas) increased with temperature, but the yield did not quite equal the Fisher assay value of 44% maf (moisture, ash free). The tar yield was relatively low, a maximum of 10.6% maf at 650°C, which does not include light hydrocarbon yield (BTX) or water.

A considerable amount of water was formed, 15-18% of coal as fed, (moisture content of coal = 10.02%), probably due to the high oxygen content of the coal. Water behaviour is shown in Fig. 10. The decrease in water yield above 650°C may be due to the water-gas reaction. An apparent maximum in water content occurs at about 600°C, about the temperature at which the rate of the water-gas reaction becomes significant.

A large amount of carbon monoxide and carbon dioxide were formed with this coal, again due to the high oxygen content. Hydrocarbon yields were relatively low over most temperatures, although methane and ethylene increased greatly above 700°C. The yields of all gases were higher in a hydrogen atmosphere, with the increase in yield of CH_4 by nearly 100% at 750°C being most noticeable.

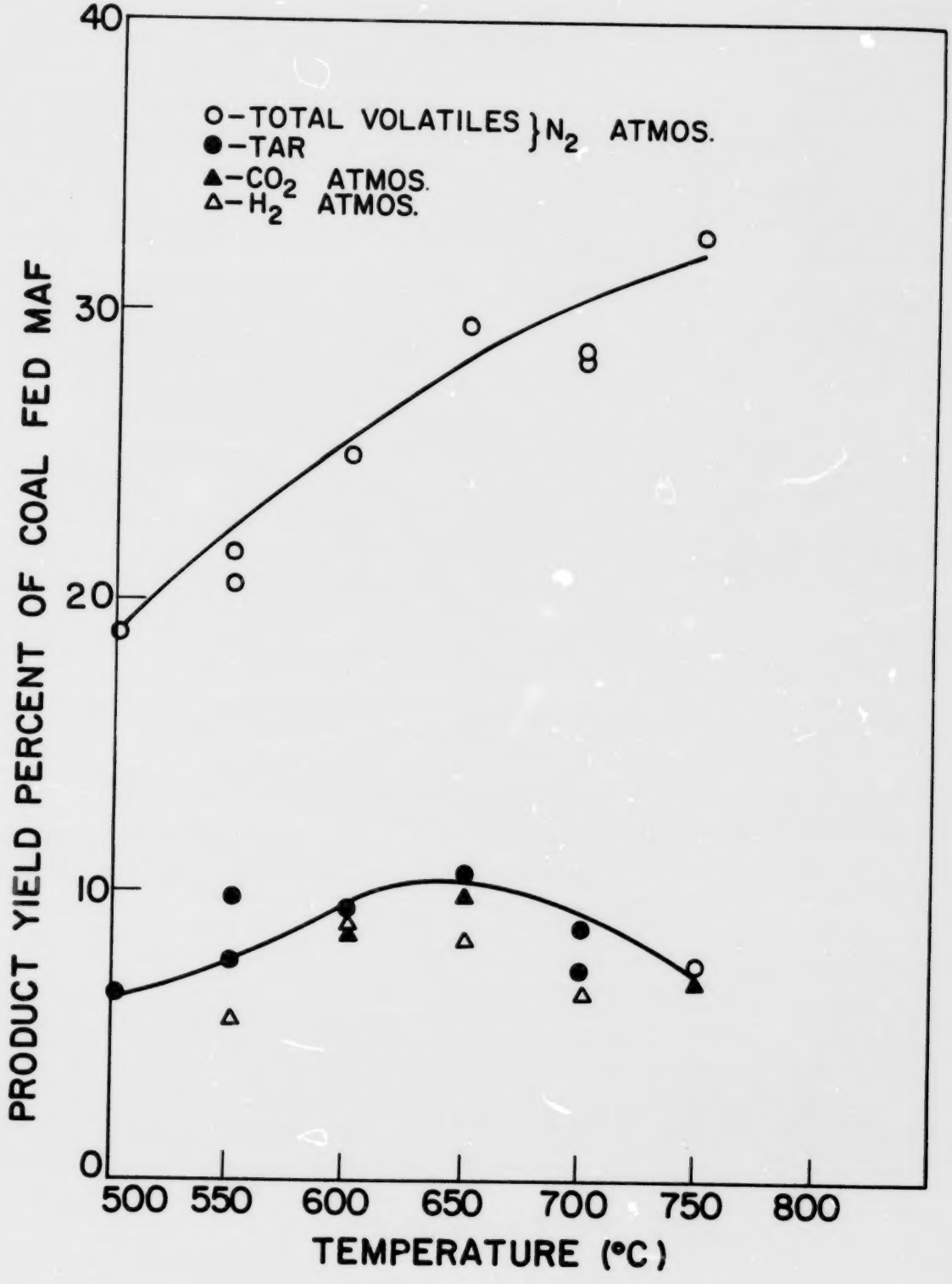


Figure 6 Forestburg Coal - Volatiles and Tar Yield, maf

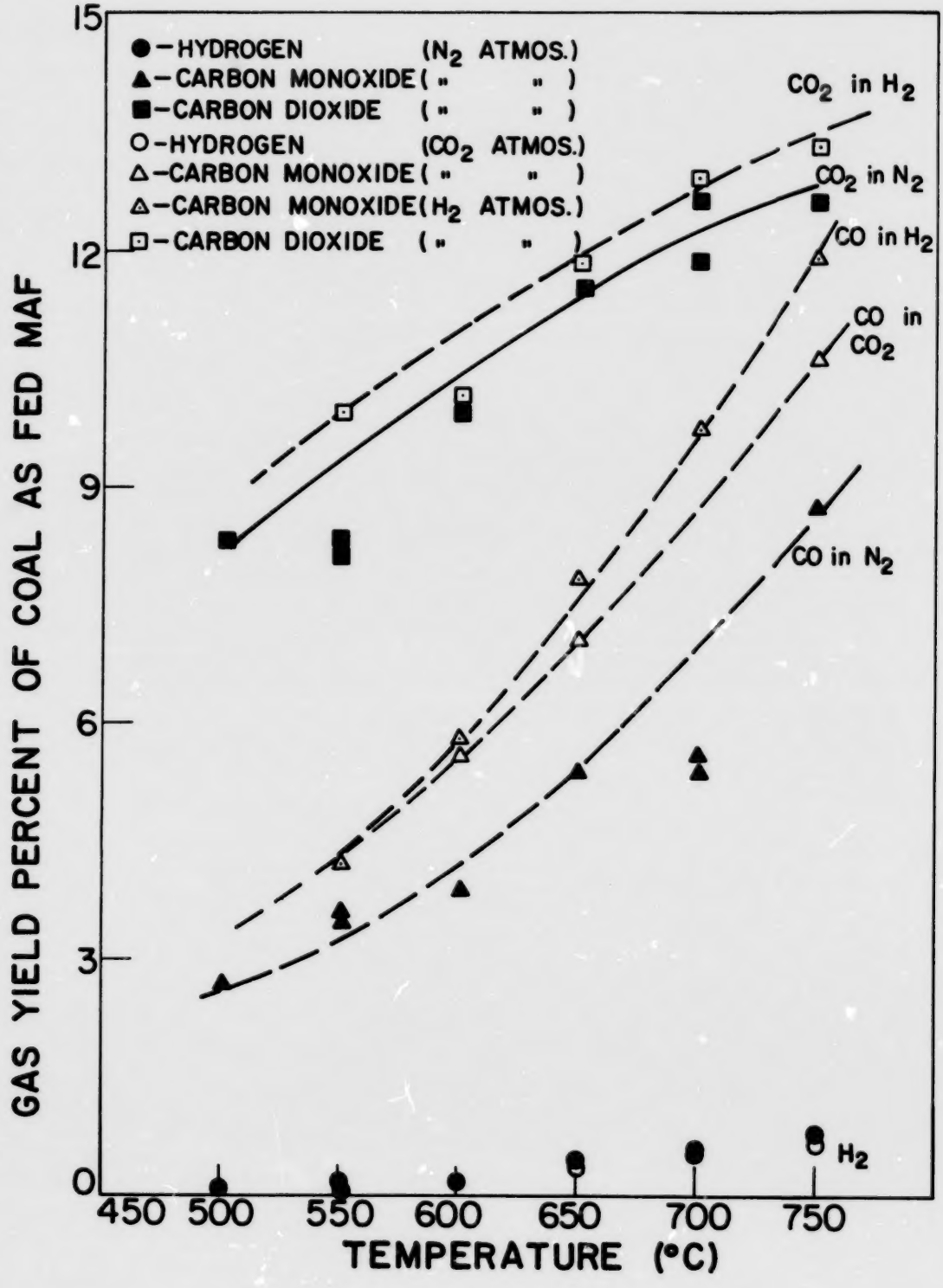


Figure 7 Forestburg Coal - Gas Yields, maf, of CO, CO_2 and H_2

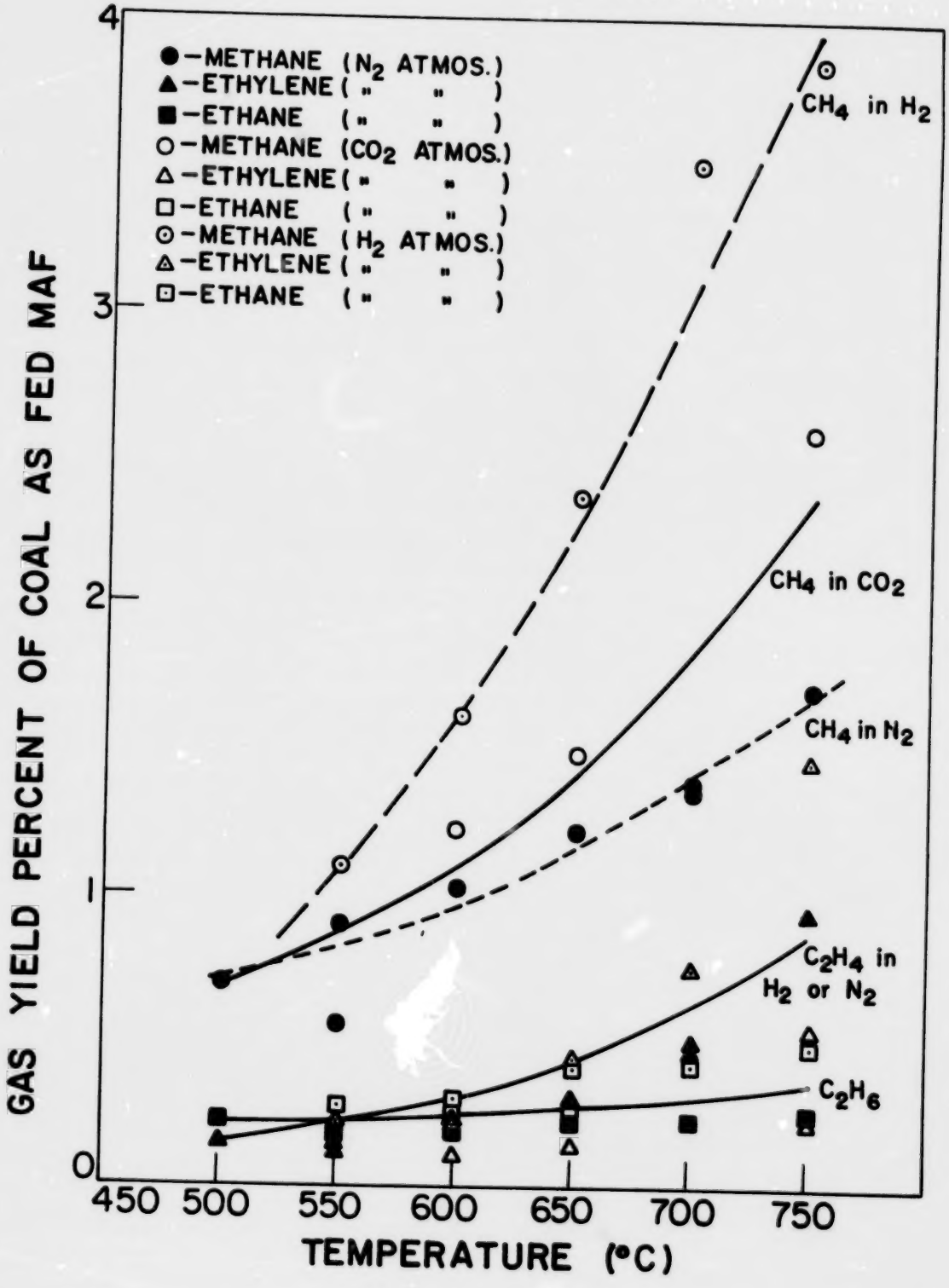


Figure 8 Forestburg Coal - Gas Yields, maf, of CH_4, C_2H_4 and C_2H_6

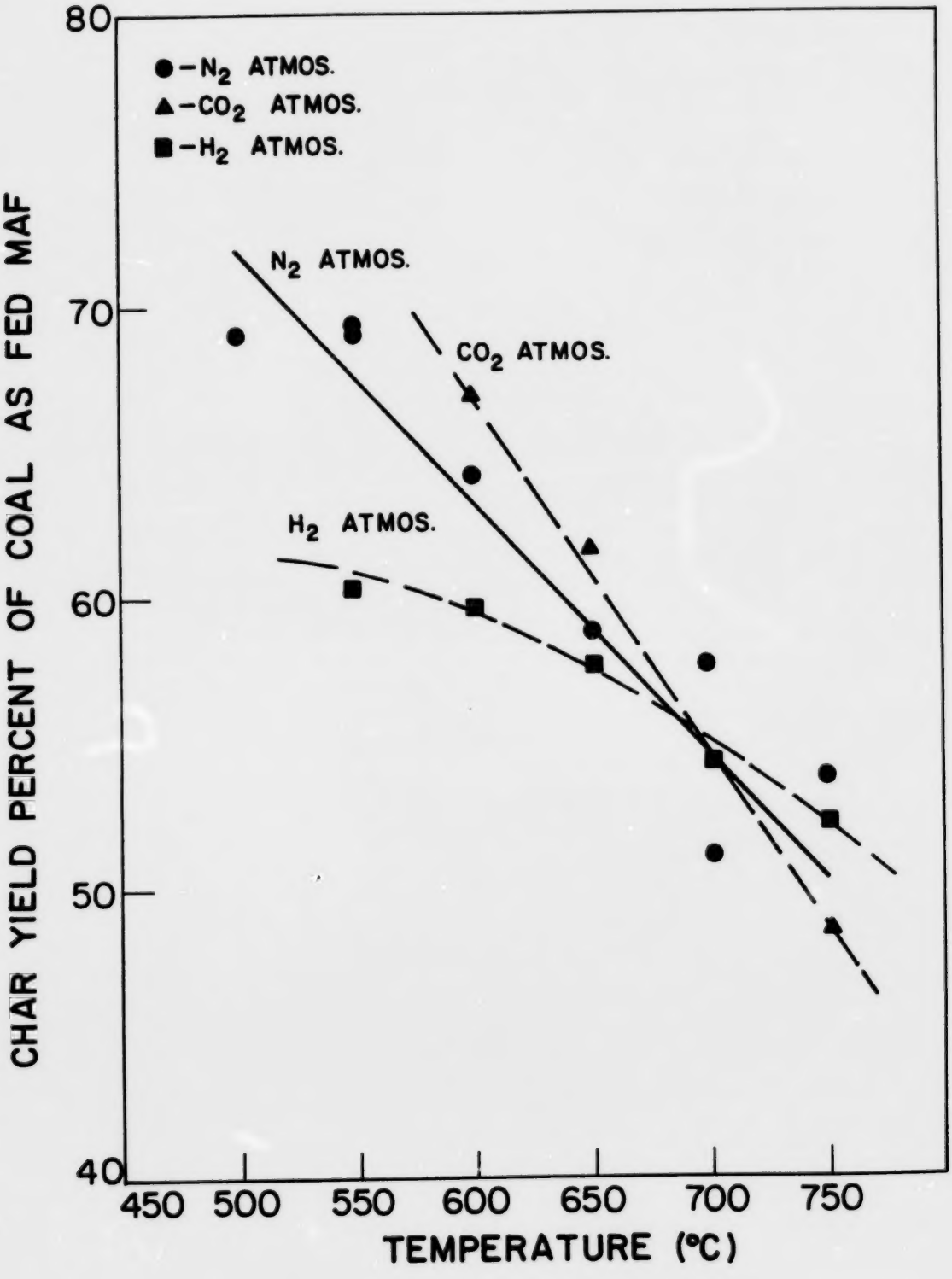


Figure 9 Forestburg Coal - Char Yields, maf

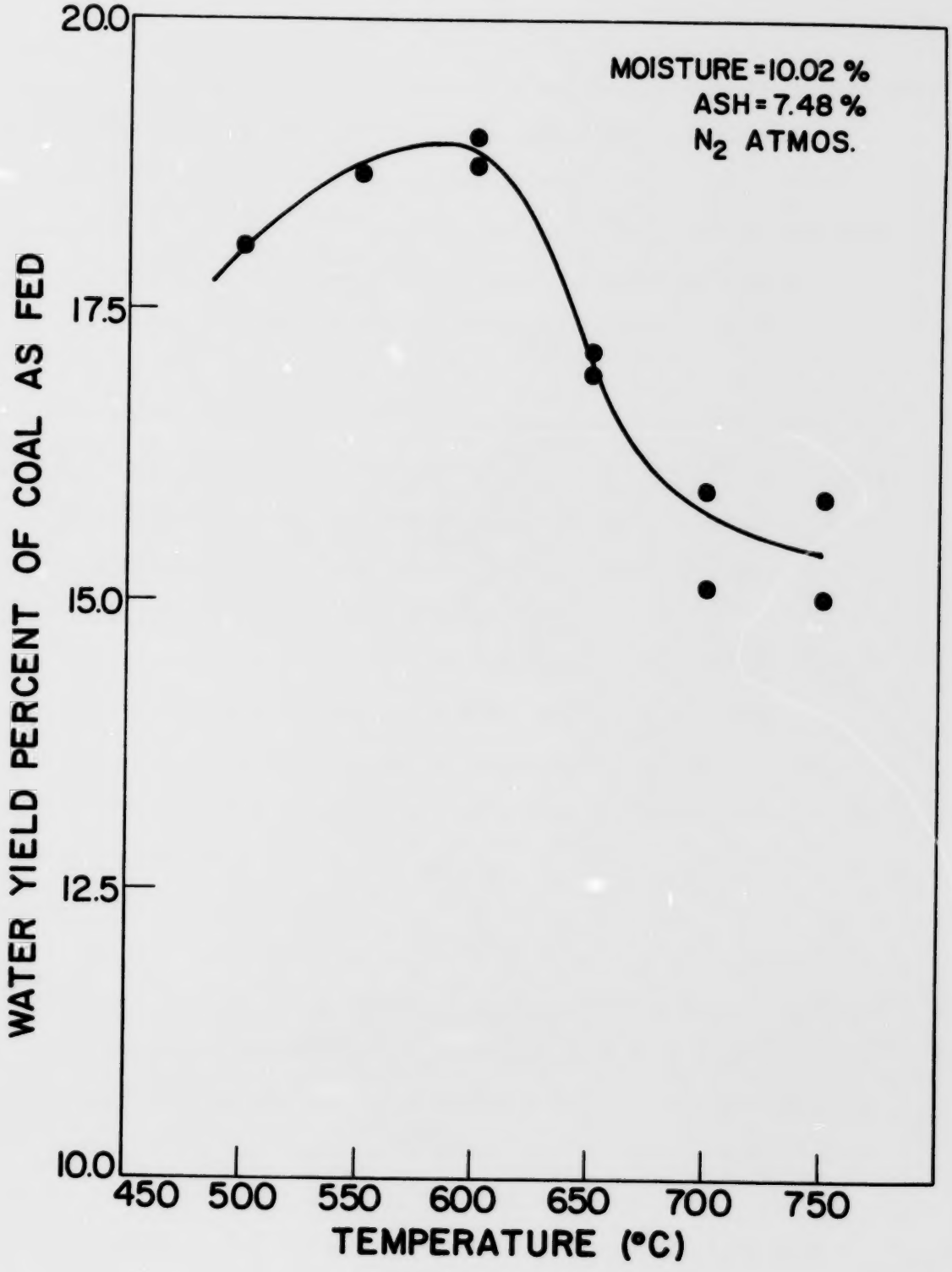


Figure 10 Forestburg Coal - Total Water Yield, maf

Fig.11 shows the relative amounts of tar dissolved by dichloromethane and acetone, and indicates that the largest amount of polar liquids (highly oxygenated) occurs at the maximum liquid yield.

Fig.12 represents char distribution, where "bed char" is that char remaining in the fluidized bed, "filter paper" is that char blown into lines and condensers, and "reactor" is that char remaining on the reactor walls.

The tests performed in a carbon dioxide atmosphere revealed no significant change in oil yield. Carbon dioxide was chosen because it has been reported to deactivate the char which can act as a cracking catalyst. The main difference observed lay in the increased yields of carbon monoxide and methane. The other hydrocarbons were not affected.

Runs 25-29 were performed in an approximately 50% hydrogen atmosphere. Tar yields were slightly lower,while gas yields increased. Char yields were similar to before. The difference in gas yields was largely due to increased carbon monoxide and carbon dioxide yields, although methane yield also increased.

Highvale Coal

The yields of volatiles and tar (excluding light hydrocarbons) are presented in Fig.13. The product gas analyses are shown in Fig.14 and 15. Char yield is shown in Fig. 16 and water produced is shown in Fig.17. Tar and char distributions are shown in Fig.18 and Fig.19 respectively.

In general, tar yields based on maf coal fed were slightly higher than for Forestburg coal (11.2% vs. 10.6% maf at the optimum). The trend in tar yield with temperature is similar for the two coals with a maximum yield being obtained at about 650°C.

Char yield from the Highvale coal is higher, at 60-77% of coal, maf basis. Gas yields, however, were somewhat lower. This difference

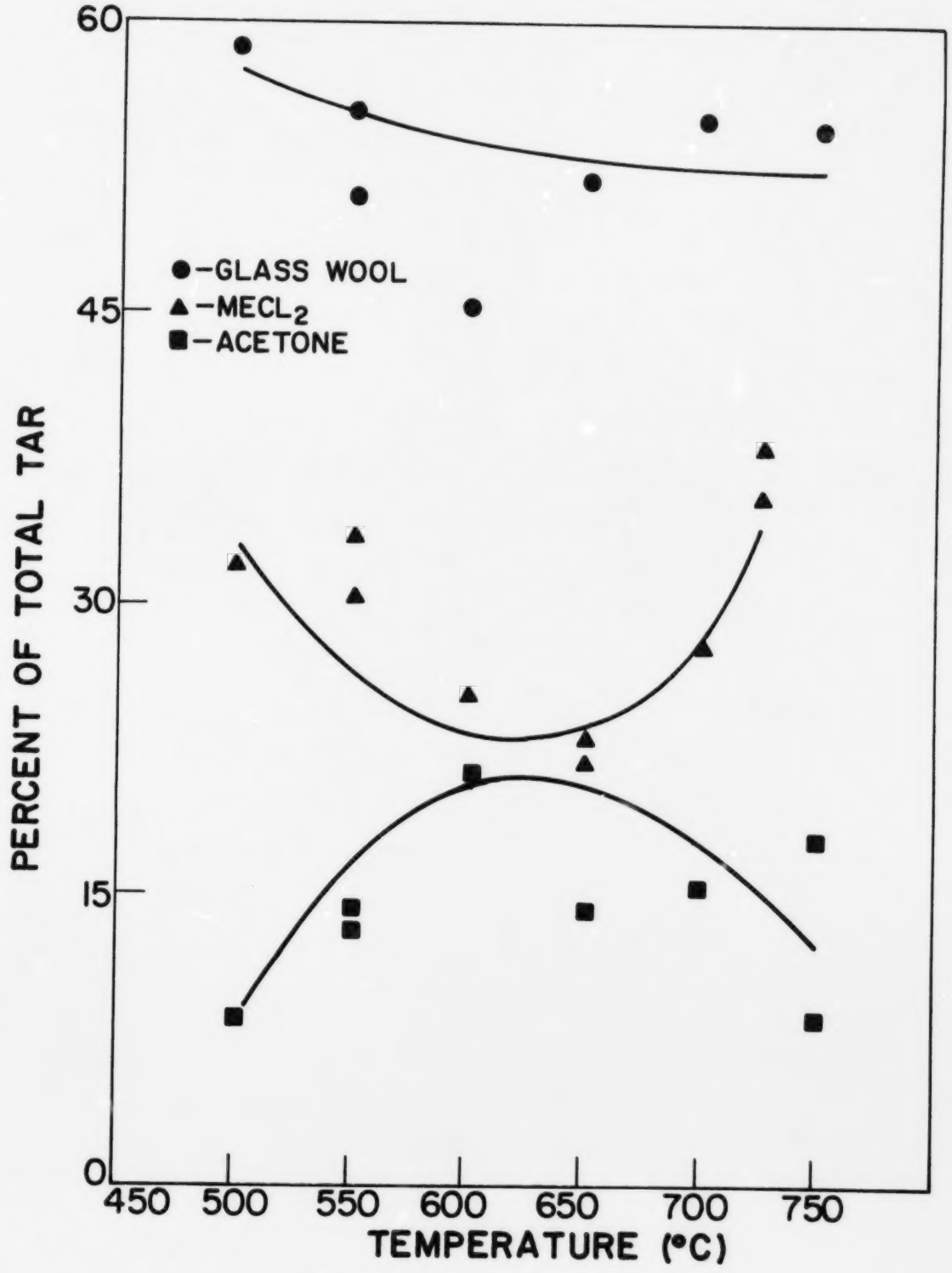


Figure 11 Forestburg Coal - Tar Distributions During Analysis

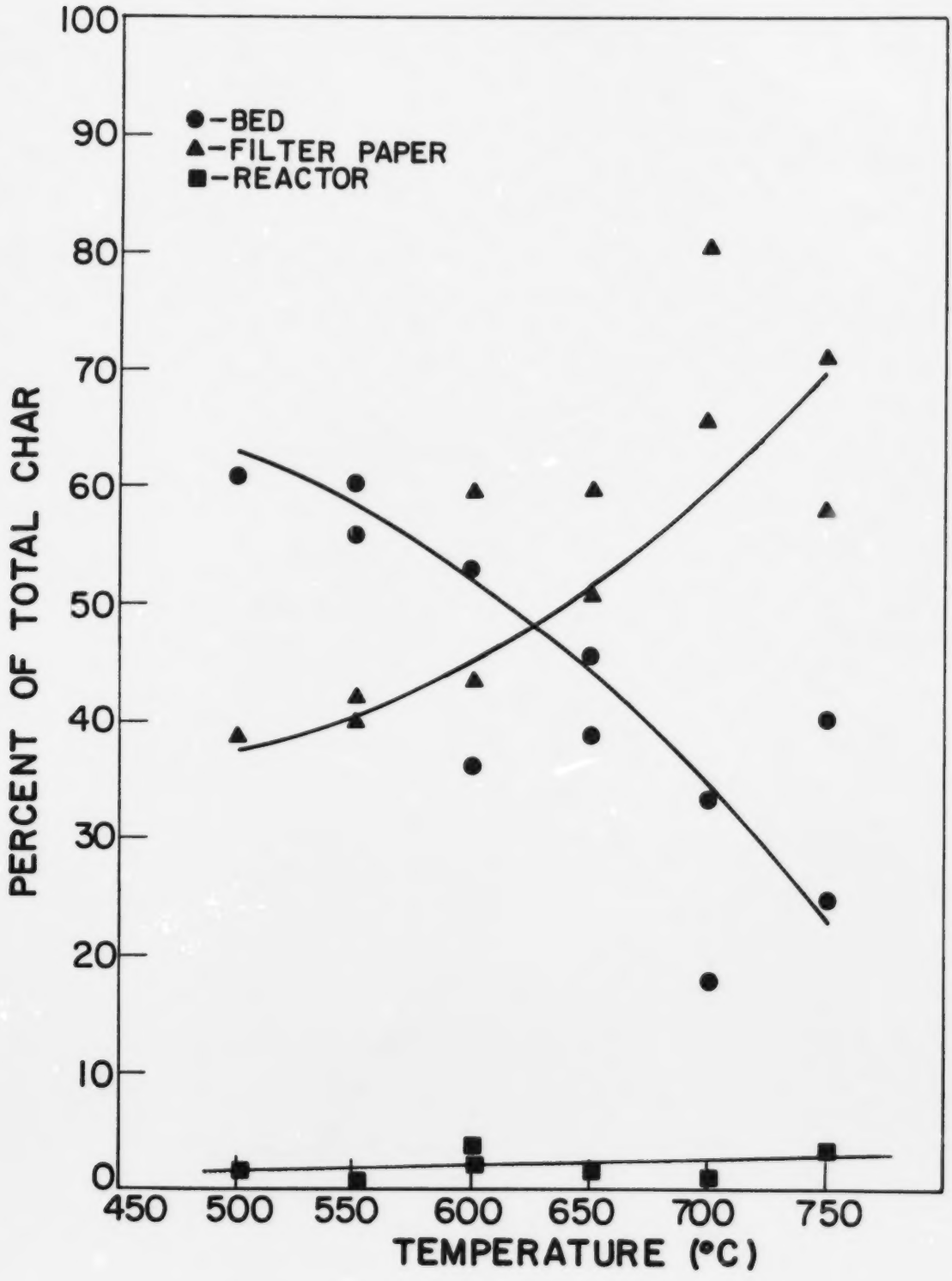


Figure 12 Forestburg Coal - Char Distribution During Analysis

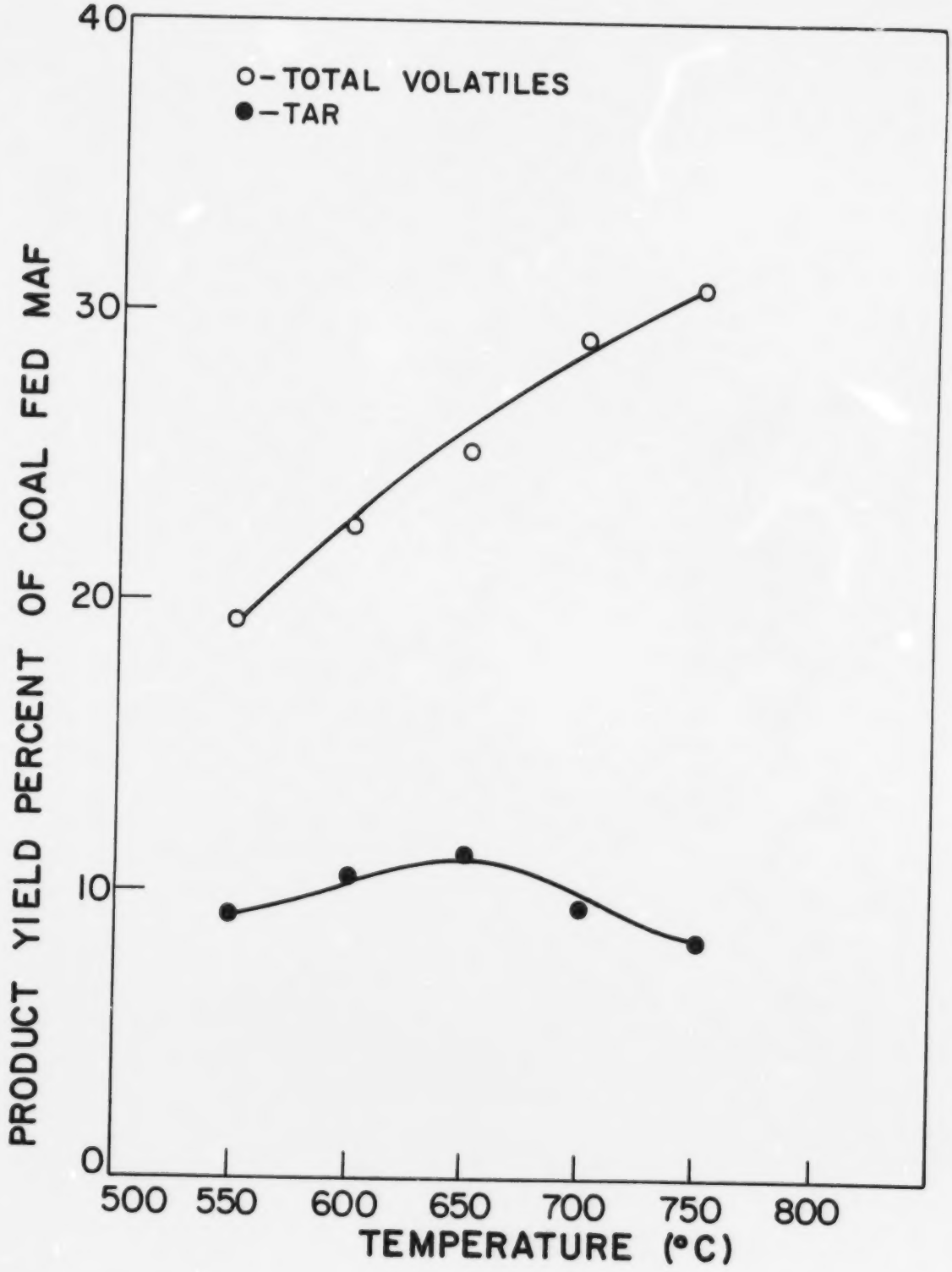


Figure 13 Highvale Coal - Volatiles and Tar Yield, maf

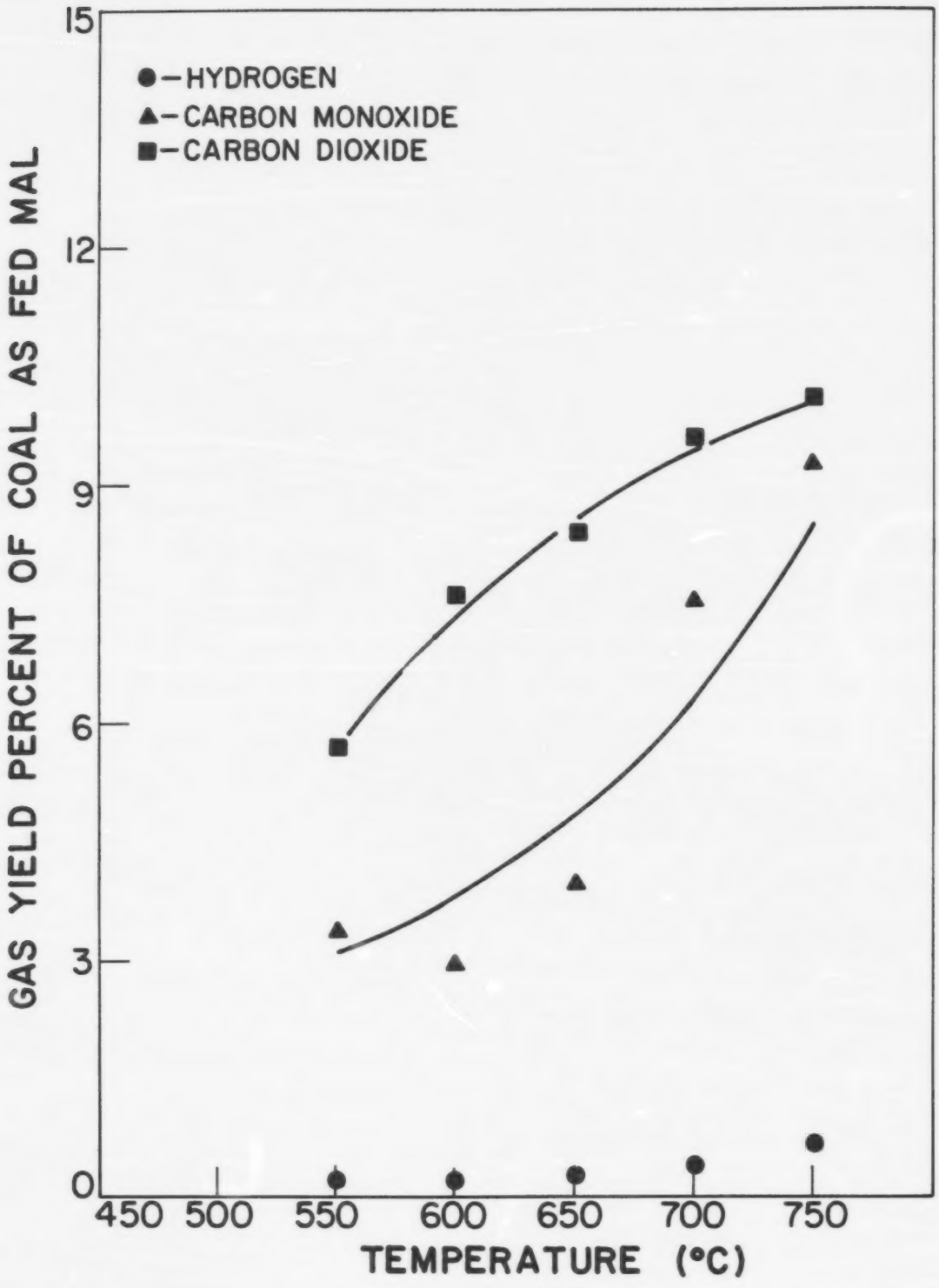


Figure 14 Highvale Coal - Gas Yields, maf, for CO, CO_2 and H_2

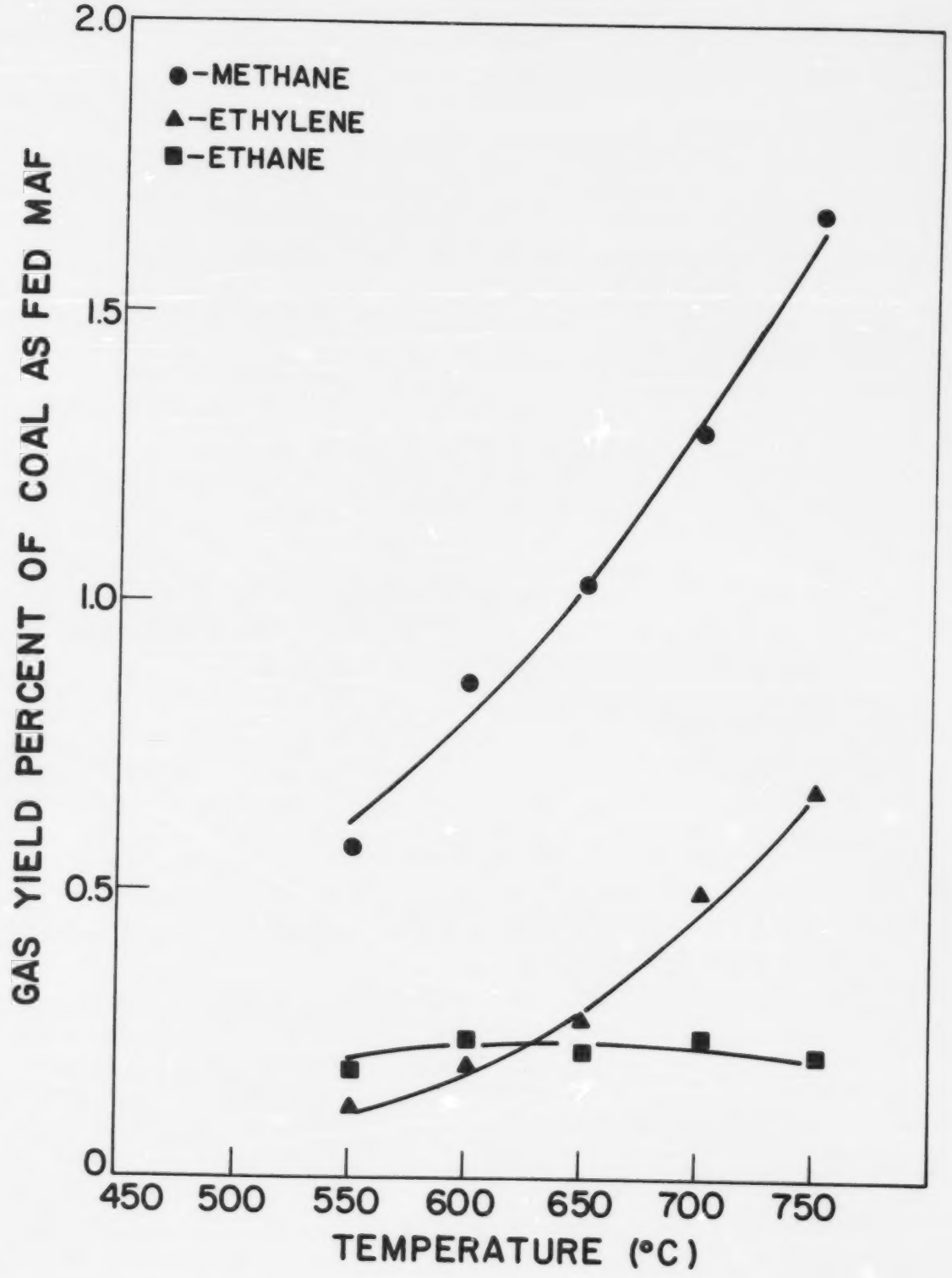


Figure 15 Highvale Coal - Gas Yields, maf, for CH_4, C_2H_4 and C_2H_6

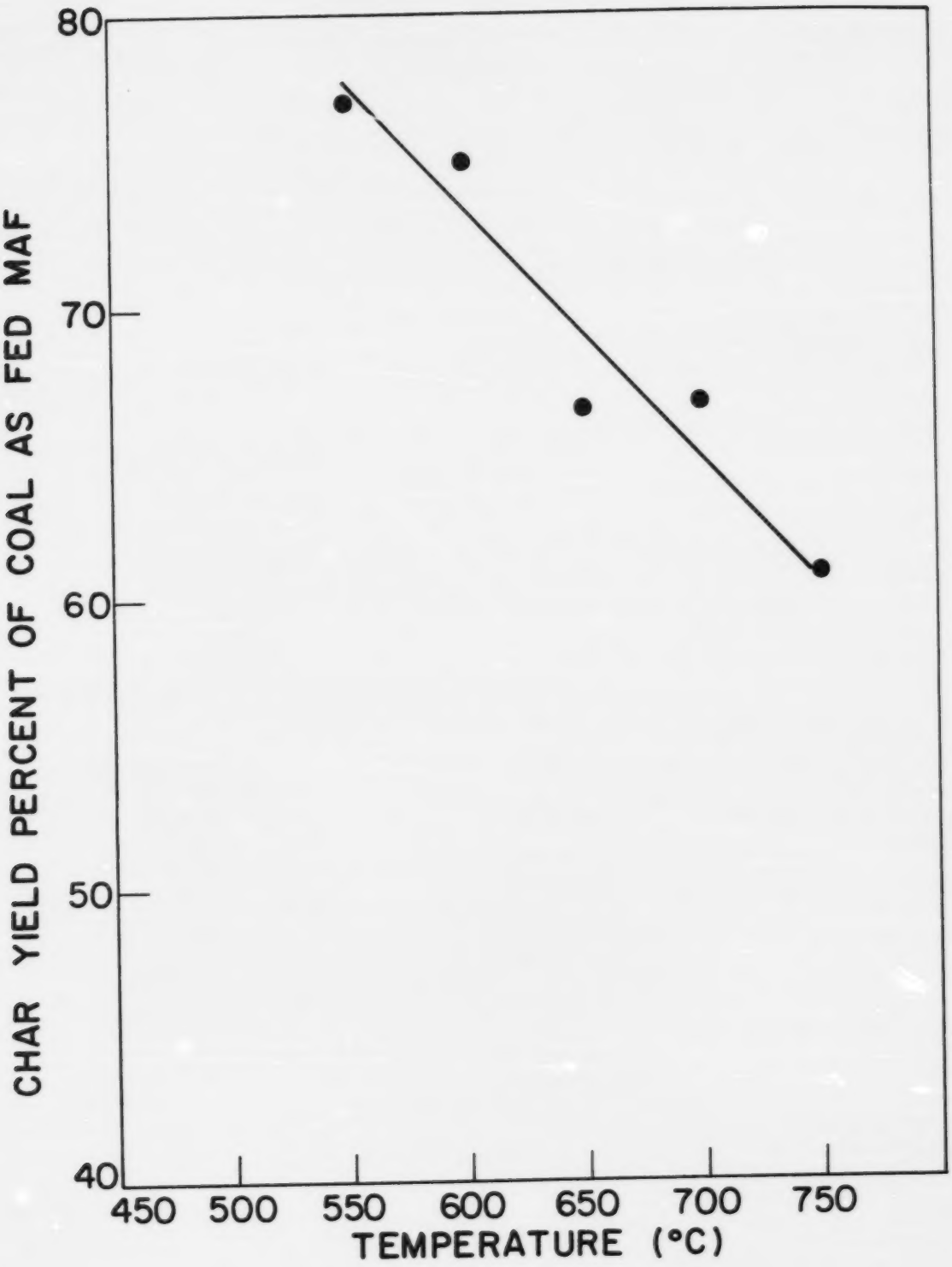


Figure 16 Highvale Coal - Char Yield, maf

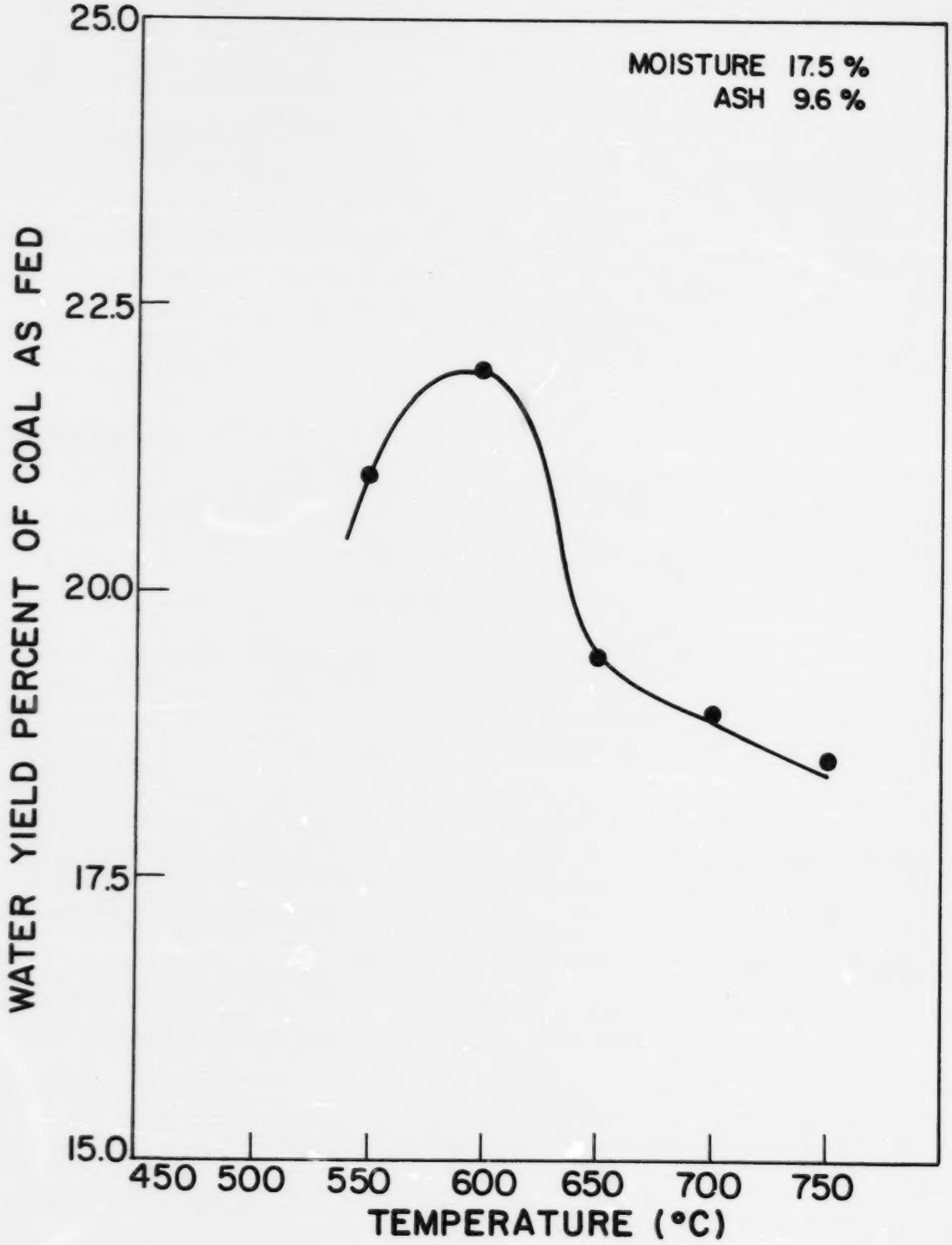


Figure 17 Highvale Coal - Total Water Yield, maf

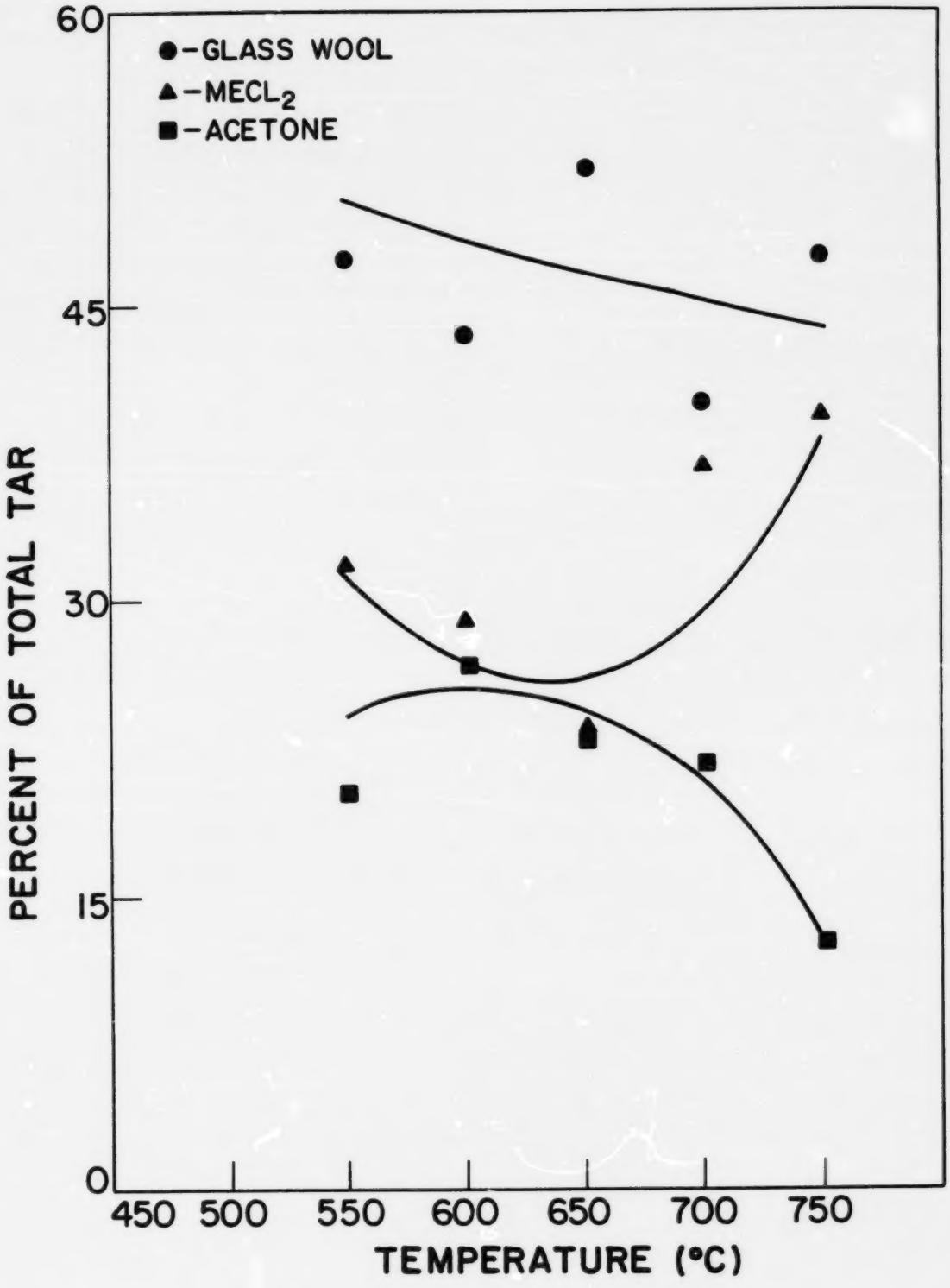


Figure 18 Highvale Coal - Tar Distribution During Analysis

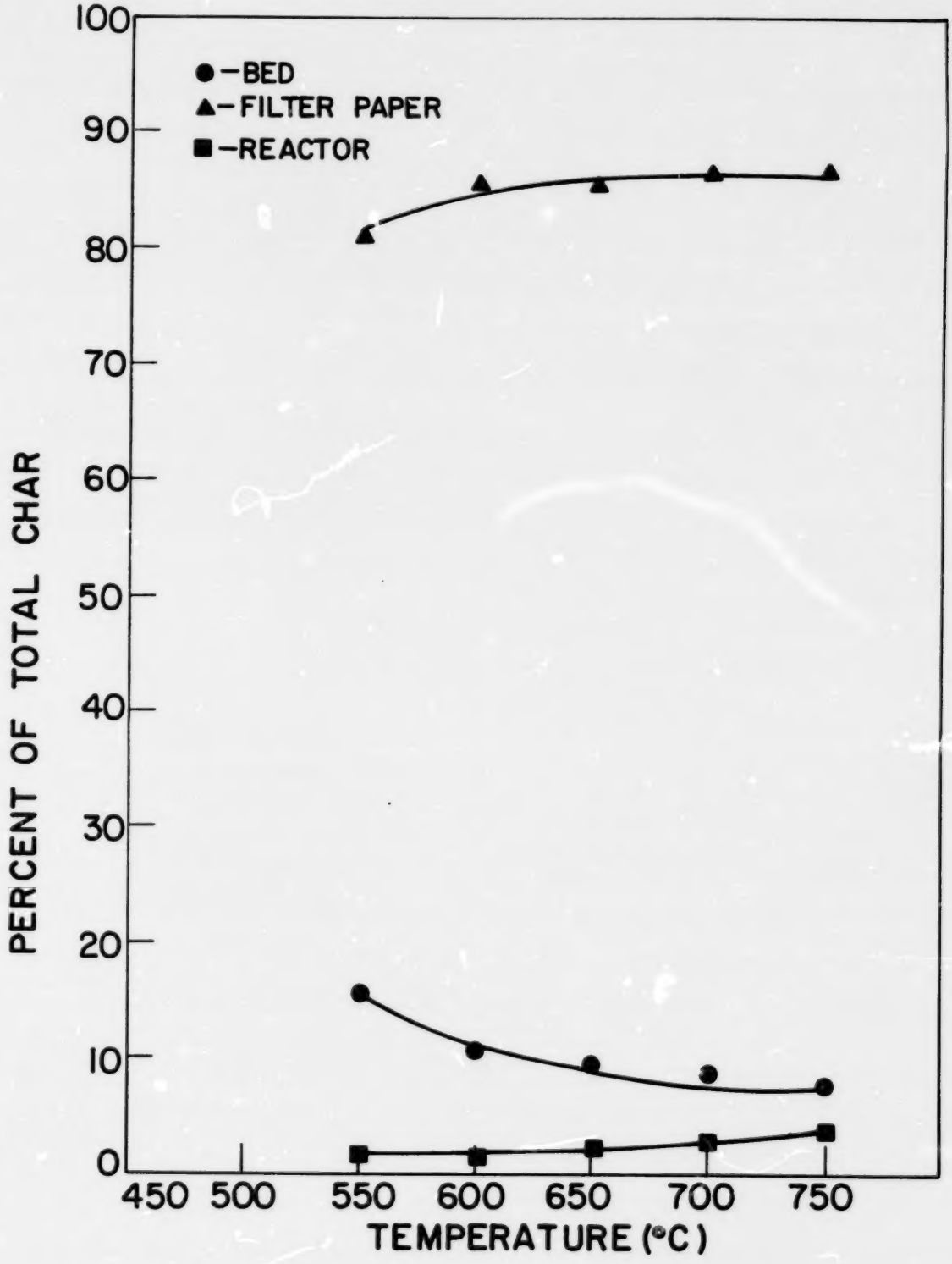


Figure 19 - Highvale Coal - Char Distribution

was largely due to decreased carbon monoxide and dioxide production. These two gases exhibited a similar behaviour, however, in both coals, though the Highvale coal yields more carbon monoxide at higher temperatures. The light hydrocarbon gases give very similar yields for both coals in nitrogen atmospheres.

As with Forestburg coal, the tar distribution seems to indicate that the maximum amount of polar liquid components occurs at maximum liquid yields.

The greatest difference in the pyrolysis behaviour of the two coals is in the char distribution. Only 10-20% of the Highvale char remained in the bed, indicating a lower density, more porous char.

Complete tabular data for both the Highvale and Forestburg coals are presented in the Appendix on both an "as fed" and "moisture and ash free basis".

BTX Yield (Forestburg and Highvale Coals

BTX yield and trends with temperature were similar for both Forestburg and Highvale coals. The yield of BTX increased only slightly over the 550-650°C temperature range, but increased greatly near the 700°C mark. The BTX yields are given in Tables 5, 6, 7 and 8 for the three different reaction atmospheres used with Forestburg coal, and for Highvale coal in a nitrogen atmosphere.

The Highvale coal yielded less than 0.75% maf basis of BTX at 750°C and averaged only 0.25% maf over the lower temperatures. Results for Forestburg coal under a carbon dioxide atmosphere yielded somewhat lower results, especially at 750°C. A significant increase, however, was observed for Forestburg coal in a 50% hydrogen atmosphere. BTX yields averaged 0.47% maf for 550-650°C and 1.28% maf at 750°C.

Table 5

BTX Yield for Forestburg Coal - Nitrogen Atmosphere

Run	Temp. (°C)	BTX Yield % of feed maf	% of tar
13	500	0.22	3.2
15	550	0.19	2.6
14	600	0.24	2.6
16	650	0.29	2.8
12	700	0.35	4.7
11	750	1.15	15.3

Table 6

BTX Yield for Forestburg Coal - CO_2 Atmosphere

Run	Temp. (°C)	BTX Yield % of feed maf	% of tar
17	600	0.21	2.4
18	650	0.23	2.4
19	750	0.56	7.9

Table 7

BTX Yield for Forestburg Coal - 50% Hydrogen Atmosphere

Run	Temp. (°C)	BTX Yield % of feed maf	% of tar
25	550	0.36	6.7
26	600	0.39	4.5
27	650	0.65	7.9
28	700	0.91	14.6
29	750	1.28	20.5

Table 8

BTX Yield for Highvale Coal - Nitrogen Atmosphere

Run	Temp. (°C)	BTX Yield % of feed maf	% of tar
20	550	0.17	1.9
21	600	0.22	2.2
22	650	0.23	2.1
23	700	0.38	4.0
24	750	0.71	8.6

Devco Coal

The initial runs on Devco coal resulted in the blockage of the coal injection tube after only a few minutes. This was not unexpected, as Devco is a caking coal. An additional run was performed using a finer mesh coal, -200 +325 mesh, and larger sand particles, -30 +60 mesh, to help prevent the agglomerate from forming. However, the coal was difficult to feed, and the blockage occurred once again. Following a redesign of the injection tube to allow gas cooling, three successful runs were carried out. Although the injection tube was no longer plugged during a run, some caking and agglomeration took place in the bed. Practically none of the char was blown out of the bed. Hence, runs had to be limited to 15 to 20 minutes.

Table 9 gives the results of runs with Devco coal, as measured based on the coal maf. Much lower gas yields and much higher tar yields at high temperatures are apparent. Yields of various gaseous components are shown in Table 10. Methane is the largest product, but the CO and CO_2 produced are a suprisingly large fraction of the total. The increase in C_3 hydrocarbons at high temperatures indicates that cracking of tar is becoming significant above 700°C.

Table 9

Yields from Devco (Cape Breton) Bituminous Coal

N_2 atomosphere, -100 +200 mesh coal, 20 grams sand -30 +60, cooled injector, Ash 2.8%, Moisture 1.2%

Run No.	37	38	39
Temperature °C	560	660	750
Gases % maf	0.48	4.55	8.39
Tar % maf	3.88	16.72	19.64
Char % maf	88.89	67.26 67.15	55.98
BTX % maf	<1.0	<1.0	≈1
Water % maf	4.78	9.41 8.55	8.77
Total	≈99	≈98	94

Table 10

Gas Yields from Devco (Cape Breton) Bituminous Coal

N_2 Atmospheres -100 +200 mesh coal, 20 grams sand -30 +60, cooled injector, Ash 2.8%, Moisture 1.2%

	Yield, % of coal fed, maf		
Run No.	37	38	39
Temperature °C	560	660	750
H_2	Trace	0.27	0.53
CO	0.13	0.93	1.93
CO_2	0.20	0.81	1.08
CH_4	0.14	1.81	2.65
C_2H_4	Trace	0.22	0.80
C_2H_6	0.02	0.51	0.60
C_3S	Trace	Trace	0.78
Total	0.49	4.55	8.77

Discussion

Only two elemental char analyses were carried out (by a commercial laboratory),and hence carbon balances are limited to these two runs. However,it is the result for carbon which appears to be significantly in error, and so these char analyses can only be used at this time for estimation. Runs on Forestburg and Highvale coals are presently being repeated to obtain additional char and tar samples for analysis in-house, now that equipment is available.

Results of the two char analyses (adjusted for carbon content by comparison of Guelph and EMR results on the same coal) are shown in Table 11. No normalizing of the material balance to 100% has been done. However, these values allow an estimate to be made for the minimum percentage of the carbon converted which appears as hydrocarbon liquids.

Some points of interest arise from the results presented graphically and in Table 9. The high gas yields from the sub-bituminous coals with a high percentage of CO and CO_2 are as expected and confirm results in the literature. At the maximum temperature of 750°C the CO and CO_2 production represents 68% of the original oxygen in the coal for the Forestburg coal, and 66% of the original oxygen for the Highvale coal. At the point of maximum liquid yield, about 56% of the oxygen in the Forestburg coal is rejected as CO and CO_2. When the oxygen rejected as water of reaction is added, over 91% of the oxygen in the original coal has been rejected at 650°C as CO, CO_2 or H_2O.

Water formed appears to be at a maximum at a temperature of 600°C for both Forestburg and Highvale coals. Most of the oxygen in the Devco coal at 600-650°C apparently goes to form water of reaction, and very little to CO_2 or CO. Further analysis of the water produced and its degree of reaction is required.

Table 11

Char Analyses, Forestburg Coal, N_2 Atmosphere

Run	16	11
Temperature °C	650	750
C %	64.61	64.76
H %	3.16	3.00
N %	1.60	1.52
* Carbon conversion%	47.2	35.2
Carbon converted to tar%	13.6	10.9
% converted carbon as tar	28.9	41.8

* not adjusted for material balance.

The BTX yield increases sharply as the temperature increased from 700°-750°C. This was accompanied by a reduction in tar yield. However, the large increase in the fraction of light hydrocarbon liquids at high temperatures suggests that a better product may be obtained at higher temperatures. Larger amounts of liquid product obtained in long duration runs would allow some additional product evaluation.

The results in a hydrogen atmosphere of about 50 k Pa partial pressure show a considerable increase in hydrocarbon gases, and a material balance consistently over 100%. This implies that a certain amount of the hydrogen has been incorporated into the product. Detailed analyses which would permit hydrogen balances to be made would show what benefit, if any, was being obtained in product quality.

In comparing the results obtained in this work to those of similar investigations reported in the literature, one problem arises. In much of the work reported, yields given have been "adjusted" to a 100% material balance using various methods, not always clearly specified. In the tests most closely analagous to this work in mini fluidized beds (for example Tyler (26) (27)) and in entrained flow atmospheric pressure reactors (for example, Forrest and van Meurs (28)), the liquid hydrocarbon yield or "tar" yield has been determined by difference. In effect, this assigns all analytical errors to the tar determination, if it is determined at all. In the present work, small errors will exist in the gas yield value, largely because gaseous nitrogen and sulphur compounds are not measured. Char values should show little error, given the method of measurement used here. The major negative errors would be in the light hydrocarbons and tar fraction; and perhaps to a lesser extent in water determination. Hence, there is some justification for determining liquid hydrocarbon yield by difference. In any event, to be comparable to published work, this is

the approach that should be used.

Table 12 gives values for the yield of oil at the point of maximum production, determine as coal fed - (char + water + gas). It can be seen that these values are somewhat higher, as expected, than those obtained by direct measurement. In addition, the Forestburg coal now shows a significantly higher yield than does the Highvale coal.

Tyler (27) has shown that for a wide variety of bituminous coals, a correlation exists between the maximum tar yields and the hydrogen/carbon ratio of the coals. When the data shown in Table 11 are plotted on the graph given by Smith (14), shown in Fig.20, the agreement is remarkably good. This suggests, as a minimum, that the work using our mini-fluidized bed reactor gives results comparable to those of the CSIRO work. Whether the higher liquid yields deduced when determined by difference are justified will not be certain until better and more complete product analyses can be done.

Table 12

Run	Temp. (°C)	Max. Oil Yield by Difference, % maf	Coal Type H/C ratio
10	700	19.0	Forestburg
12	700	17.9	H/C = 0.75
22	650	14.0	Highvale
23	700	13.5	H/C = 0.65
39	750	26.8	Devco H/C = 0.79

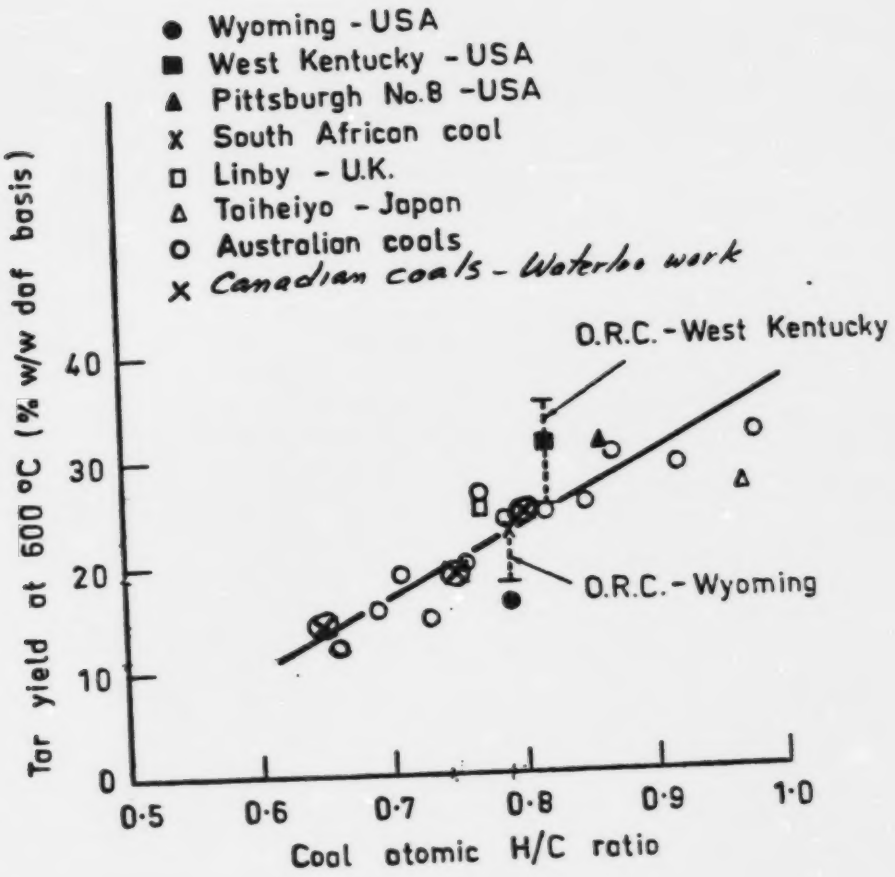


FIG.20 DEPENDENCE OF TAR YIELD AT 600 °C ON COAL ATOMIC H/C RATIO (BITUMINOUS COALS)
(From Smith (14))

Figure 20 Comparison of Present Results with CSIRO Correlation of Maximum Tar Yields

REFERENCES

(1) "An Investigation of the Short Residence Time Pyrolysis of Coal" D.S. Scott, Dept. of Chemical Engineering, University of Waterloo, Final Contract Report to Energy Research Laboratories, CANMET, July 10th, 1980, Contract OSU 79 - 00190.

(2) "Hydropyrolysis of Alberta Forestburg Sub-Bituminous Coal" J. A. Hamshar , D.P. Rimmer, W.A. Fling and D.R. Kahn, "2nd World Congress of Chem. Eng., Montreal, Oct. 6th, 1981, Paper 9.11.5.

(3) "The CANMET Program on Coal Pyrolysis - Application to Eastern Canada" S. Fouda, presented at conference "Application of Pyrolysis Technology to the Utilization of Eastern Canadian Coals" Atlantic Research Lab., NRC. Fredericton, N. B. Jan. 5-6, 1982 (Proceedings to be published by ARL)

(4) "Utility Perspectives and Interests" J. R. Thurgood, Proc. EPRI Conf. on Coal Pyrolysis, Palo Alto, Feb. 25, 1981.

(5) "The Utah Char-Oil Project" J. R. Thurgood, presented at AICHE Spring Meeting, Orlando, Fla. Feb. 28, 1982.

(6) "Production of Syncrude from Coal using the Toscoal Pyrolysis Process" D.H. Cortez , C.J. LaDelfa, presented at AICH E Spring Meeting, Orlando, Fla. Feb. 28, 1982.

(7) "Lurgi Coal Pyrolysis for the Production of Synthetic Fuels" R.W. Rammler, presented at AICH E Spring Meeting, Orlando, Fla. Feb. 28, 1982.

(8) "Rapid Pyrolysis and Hydropyrolysis of Canadian Coals" P.C. Stangeby and P.L. Sears, Fuel, 60, 131-135, (1981)

(9) "Short Residence Time Atmospheric Pressure Pyrolysis of Canadian Coals, Part 2", D.S. Scott, Final Contract Report, CANMET OSU 81 - 00087, June, 1982.

(10) "Pyrolysis of High Volatile Bituminous Atlantic Coals", E. Chornet, Dept. of Applied Science, University of Sherbrooke, Contract Report, (1981)

(11) "Development of an Integrated Research and Development Program on Eastern Canadian Coals" ARL Tech. Report 27, NRCC 19539, 1981, prepared by D. Abbott, Research and Productivity Council, New Brunswick.

(12) "Technical Assessment of Coal Liquefaction Processes for Canada, Vol. 5, CS/R Flash Hydropyrolysis Process" Tech Development Dept., SNC Group, Montreal, N.E. Cooke, Project Manager, June, 1981, (Draft Report to Energy, Mines and Resources).

(13) "The Pyrolysis of Canadian Coals for the Production of Fuels and Petrochemicals" E. Furimsky, R. Belanger and J. Jorgensen, presented at ARL Workshop "Application of Pyrolysis Technology to the Utilization of Eastern Canadian Coals" Fredericton, N.B., Jan 5-6, 1982.

(14) "Australian Research on Flash Pyrolysis" I.W. Smith, AICH E Spring Meeting, Orlando, Fla., Feb. 28th, 1982.

(15) "Effects of Calcium Minerals on the Rapid Pyrolysis of a Bituminous Coals" H.D. Franklin, W.A. Peters, F.Cariello, and J.B. Howard, Ind. Eng. Chem. Process Des, Devel., 20, 670-74, (1981)

(16) "Mineral Matter Effects on the Rapid Pyrolysis and Hydropyrolysis of a Bituminous Coal 1. Effects on Yields of Char, Tar and Light Gaseous Volatiles" H.D. Franklin, W.A. Peters and J.B. Howard, Fuel, 61, 155-160, (1982)

(17) "Flash Pyrolysis of Coals; Influence of Cations on the Devolatilization Behaviour of Brown Coals" R.J. Tyler and H.N.S. Schafer, Fuel 59, 487, (1980).

(18) "Flash Pyrolysis of Wyodak Coal" S.C. Che, K. Durai-Swamy, C.B. Chen and G.E. Dolbear, presented at AICH E Spring Meeting, Orlando, Fla., Feb. 28, (1982)

(19) "Bibliography of Coal Pyrolysis, 1980-1981" Atlantic Research Laboratory, National Research Council of Canada, Fredericton, 1982 D. Abbott, Manager, Energy Projects

(20) "Model of Coal Pyrolysis 1. Qualitative Development" G.R.Gavalas, P.H-K. Cheong and R. Jain, Ind. Eng. Chem. Fund. 20, 113-121, (1981)

(21) "Model of Coal Pyrolysis 2. Quantitative Formulation and Results" G.R. Gavalas, R. Jain and P. H-K Cheong, I.E.C.Fund, 20, 122-131 (1981)

(22) "Pyrolytic Desulfurization of Coal in Fluidized Beds of Calcined Dolomite" J.D. Yeboah, J.P. Longwell, J.B. Howard and W.A. Peters. Ind. Eng. Chem. Proc. Des. Devel. 21, 324-330, (1982)

(23) "Effects of Preoxidation on Pyrolysis Behavior and Resultant Char Structure of Caking Coals" D.J. Maloney and R.G. Jenkins. ACS Div. of Fuel Chem. Preprint, Vol. 27, No. 1, 25-30, (1982) Las Vegas.

(24) "An Entrained Flow Reactor with FTIR Analysis" P.R. Solomon and D.G. Hamblen, ACS Div. Fuel Chem. Preprint Vol. 27, No. 1, 41-49 (1982) Las Vegas

(25) "Coal Pyrolysis at High Temperature and Pressures" S.S. Tamhaskar, J.T. Sears and C.Y. Wen, ACS Div. Fuel Chem. Preprint Vol. 27, No. 1, P. 50-56, (1982), Las Vegas

(26) "Flash Pyrolysis of Coals: Devolatilization of a Victorian Brown Coal in a Small Fluidized Bed Reactor" R.J. Tyler, Fuel , 58, 680, (1979).

(27) "Flash Pyrolysis of Coals: Devolatilization of Bituminous Coals in a Small Fluidized Bed Reactor", R.J. Tyler, Fuel, 59, 218, (1980)

(28) "Laboratory Studies of the Rapid Pyrolysis and DeSulphurization of a Texas Lignite", R.S. Torrest and P. Van Meurs, Fuel, 59, 458, (1980).

APPENDIX

1. Sample Data Sheet

2. Tabular Results for Forestburg and Highvale Coal

16 Date FEB. 18, 1982

Run Type AIR DRIED FORESTBURG COAL (-100 +200 MESH) N_2 ATM

Run Temperature 650 °C

1. Before Run

a) Bed OTTAWA SAND (-60 +100 MESH)

b) Fluidization Rate: 490 mls/min

Dusty Gas Rate: 450 + 50 mls/min

c) Stirring Speed: 250 RPM

d) Drying Column Weight

After — g

Before — g

Water — g

e) Glass Wool Column

After 71.0 g

Before 70.4 g

Tar 0.6 g

f) Feeder Weight

After 915.0 g

Before 925.3 g

Feed 10.3 g

g) $MeCl_2$ Solubles

After 254.66 g

Before 254.45 g

Tar 0.21 g

h) Acetone Solubles

After 240.53 g

Before 240.44 g

Tar 0.09 g

i) Filter Paper Weight

After 4.60 g

Before 1.62 g

Char 2.98 g

j) Reactor Weight

After 430.2 g

Before 430.1 g

Char 0.1 g

k) Char in Fluidized Bed

Bed Wt. After 17.7 g

Bed Wt. Before 15.0 g

Char 2.7 g

2. During Run

a) Time of Run 37 min.

b) Comments

After Run

a) Total Coal Feed 10.3 g

b) Weight of char; Reactor Walls 0.1 g

Filter Paper 2.98 g

Fluidized Bed 2.70 g

Total Char 5.78 g

c) Weight of Liquid (Tar)

$MeCl_2$ Solubles 0.21 g

Acetone Solubles 0.09 g

Glass Wool Column 0.60 g

Total Tar 0.90 g

d) Weight of Light Organics -- g

Total Organics .025 g

e) Weight of Water — g

Total Liquid 1.75 g

f) Moisture Content of Solid Feed 10.02 %

4) Gas Chromatograph Analysis; 25°C, 760 mmHg

Volume of N_2 36.63 ℓ

Volume of N_2 + Gases from Pyrolysis 38.13 ℓ

Component	% Volume (G.C)	Volume [ℓ]	% Volume (N_2 free basis)	Density [g/ℓ]	Mass [g]	% of Feed
H_2	0.99	0.378		0.0826	0.031	0.303
CO	1.03	0.394		1.1442	0.450	4.370
CO_2	1.41	0.539		1.8182	0.979	9.510
CH_4	0.41	0.155		0.6622	0.102	0.995
C_2H_4	0.059	0.023		1.1494	0.026	0.252
C_2H_6	0.044	0.017		1.2270	0.021	0.200
C_3H_6 } C_3H_6	—	—	—	1.7678	—	—
Total	3.94	1.506			1.609	15.62

5) Total Yields

Component	Weight [g]	Percentage of Feed [%]
a) Gases	1.609	15.62
b) TAR	0.90	8.74
c) Char	5.78	56.12
d) Light Organics	0.025	0.24
e) Water	1.75	17.10
f) Total	10.06	97.82

TABLE E-1

Product Yield - Forestburg Coal, Nitrogen atmosphere
(based on coal as fed)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total* Excl BTX, N.S. gases
13	500	10.2	5.5	64.4	18.1	98.2
9	550	9.9	8.2	64.4	18.7	101.2
15	550	10.7	6.3	64.8	18.7	100.5
14	600	13.0	7.7	60.3	19.0	100.1
16	650	15.6	8.7	56.1	17.1	97.5
10	700	16.2	7.4	49.5	15.9	89.0
12	700	17.1	6.0	55.3	15.1	93.6
11	750	21.0	6.2	51.4	15.8	94.3

TABLE E-2

Product Yield - Forestburg Coal, CO_2 atmosphere
(based on coal as fed)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total*
17	600	6.0	7.0	62.9	18.7	94.7
18	650	7.7	8.0	58.6	16.9	91.2
19	750	12.6	5.8	47.6	15.0	81.0

* "Total" column in Tables E-1 to E-8 inclusive does not include BTX, or S or N gases produced.

TABLE E-3

Product Yield - Forestburg Coal, 50% Hydrogen atmosphere
(based on coal as fed)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total
25	550	12.9	4.5	57.2	29.7	104.3
26	600	15.4	7.3	56.4	26.8	105.9
27	650	19.3	6.8	55.2	24.6	105.9
28	700	23.2	5.2	52.4	20.0	100.8
29	750	26.1	5.4	50.2	19.4	101.1

TABLE E-4

Product Yield - Highvale Coal, Nitrogen atmosphere
(based on coal as fed)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total
20	550	7.3	6.7	65.8	21.0	100.7
21	600	8.9	7.6	64.3	21.9	102.6
22	650	10.3	8.1	58.1	19.4	95.9
23	700	14.4	6.9	58.2	18.9	98.4
24	750	16.5	6.1	53.8	18.5	95.0

TABLE E-5

Product Yield - Forestburg Coal, Nitrogen atmosphere
(maf basis)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total
13	500	12.3	6.6	69.0	9.8	97.8
9	550	12.0	9.9	69.0	10.5	101.4
15	550	13.0	7.6	69.4	10.5	100.6
14	600	15.8	9.3	64.1	10.9	100.1
16	650	18.9	10.6	58.9	8.5	97.0
10	700	19.7	8.9	51.0	7.1	86.7
12	700	20.8	7.3	58.0	6.1	92.2
11	750	25.4	7.5	53.2	7.0	93.1

TABLE E-6

Product Yield - Forestburg Coal, CO_2 atmosphere
(maf basis)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total
17	600	7.3	8.5	67.2	10.6	93.6
18	650	9.3	9.7	61.9	8.4	89.3
19	750	15.3	7.0	48.6	6.1	77.0

TABLE E-7

Product Yield - Forestburg Coal, 50% Hydrogen atmosphere
(maf basis)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total
25	550	15.6	5.5	60.3	23.9	105.3
26	600	18.7	8.8	59.2	20.3	107.0
27	650	23.2	8.2	57.7	17.9	107.0
28	700	28.9	6.5	54.2	12.6	102.2
29	750	30.5	6.7	52.1	12.2	101.5

TABLE E-8

Product Yield - Highvale Coal, Nitrogen atmosphere
(maf basis)

Run	Temp.(°C)	Gas	Tar	Char	Moisture	Total
20	550	10.0	9.2	77.0	4.8	101.0
21	600	12.2	10.4	75.0	6.1	103.6
22	650	14.1	11.2	66.5	2.7	94.4
23	700	19.8	9.5	66.6	1.9	97.8
24	750	22.7	8.3	60.7	1.4	93.1

TABLE E-9

Product Gas ~~Analysis~~ Yield - Forestburg Coal
(based on coal as fed)

Run	Temp.(°C)	H2	CO	CO2	CH4	C2H4	C2H6
13	500	0.06	2.24	6.95	0.58	0.14	0.19
9	550	0.00	2.77	6.47	0.45	0.10	0.14
15	550	0.09	2.67	6.90	0.74	0.13	0.22
25	550	--	3.30	8.30	0.91	0.18	0.22
14	600	0.10	3.22	8.50	0.85	0.18	0.17
17	600	0.09	4.63	--	1.02	0.09	0.20
26	600	--	4.71	8.90	1.35	0.18	0.24
16	650	0.30	4.37	9.51	0.99	0.25	0.20
18	650	0.20	5.92	--	1.23	0.13	0.20
27	650	--	6.80	9.87	1.97	0.37	0.28
10	700	0.29	4.33	9.87	1.14	0.41	0.20
12	700	0.32	4.50	10.65	1.12	0.38	0.18
28	700	--	8.40	10.90	2.93	0.64	0.28
11	750	0.81	7.22	10.51	1.43	0.79	0.21
19	750	0.70	9.12	--	2.15	0.48	0.19
29	750	--	10.10	11.20	3.20	1.21	0.40

TABLE E-10

Product Gas ~~Analysis~~ Yield - Highvale Coal
(based on coal as fed)

Run	Temp.(°C)	H2	CO	CO2	CH4	C2H4	C2H6
20	550	0.08	2.41	4.16	0.42	0.09	0.14
21	600	0.13	2.12	5.72	0.62	0.15	0.18
22	650	0.14	2.91	6.07	0.76	0.20	0.16
23	700	0.31	5.61	7.03	0.95	0.36	0.18
24	750	0.50	6.80	7.36	1.23	0.50	0.15

TABLE E-11

Product Gas ~~Analysis~~ Yield - Forestburg Coal (maf basis)

Run	Temp.(°C)	H2	CO	CO2	CH4	C2H4	C2H6
13	500	0.07	2.71	8.42	0.70	0.17	0.23
9	550	0.00	3.36	7.84	0.55	0.13	0.17
15	550	0.10	3.23	8.37	0.90	0.15	0.26
25	550	--	3.99	10.04	1.10	0.22	0.27
14	600	0.13	3.91	10.31	1.03	0.22	0.20
17	600	0.11	5.61	--	1.23	0.11	0.24
26	600	--	5.70	10.77	1.63	0.22	0.29
16	650	0.37	5.30	11.52	1.21	0.30	0.24
18	650	0.24	7.17	--	1.49	0.16	0.24
27	650	--	8.23	11.94	2.38	0.45	0.34
10	700	0.35	5.24	11.96	1.38	0.50	0.24
12	700	0.38	5.46	12.90	1.36	0.46	0.21
28	700	--	10.16	13.19	3.55	0.77	0.34
11	750	0.98	8.75	12.74	1.73	0.95	0.25
19	750	0.85	11.05	--	2.61	0.58	0.24
29	750	--	12.22	13.55	3.87	1.46	0.48

TABLE E-12

Product Gas ~~Analysis~~ Yield - Highvale Coal (maf basis)

Run	Temp.(°C)	H2	CO	CO2	CH4	C2H4	C2H6
20	550	0.11	3.31	5.70	0.57	0.13	0.19
21	600	0.17	2.91	7.85	0.86	0.20	0.24
22	650	0.20	3.99	8.33	1.04	0.28	0.22
23	700	0.42	7.70	9.64	1.30	0.50	0.25
24	750	0.69	9.33	10.10	1.68	0.69	0.21

TABLE E-13

Tar and Char Disribution - Forestburg Coal

Run	Temp.(°C)	TAR DISRIBUTION MECL2	ACET	G.WOOL	CHAR DISTRIBUTION BED	F.PAPER	REACT.
13	500	32.2	8.5	59.3	60.4	38.2	1.5
9	550	30.6	13.9	55.6	60.0	40.0	0.0
15	550	34.8	14.5	50.7	56.2	43.1	0.7
25	550	44.4	12.2	43.4	61.2	37.0	1.8
14	600	45.6	19.3	35.1	53.7	44.0	2.2
17	600	32.3	22.6	45.2	36.1	60.3	3.6
26	600	20.2	20.7	59.1	57.6	40.1	2.3
16	650	23.3	10.0	66.7	46.7	51.5	1.7
18	650	21.8	14.1	64.1	38.7	60.4	0.9
27	650	27.1	20.8	52.1	51.0	47.7	1.3
10	700	28.1	15.7	56.2	17.5	81.6	0.8
12	700	28.2	15.5	56.3	33.7	66.3	0.0
28	700	34.4	18.7	46.9	63.5	34.1	2.4
11	750	35.6	8.9	55.6	40.0	57.4	2.7
19	750	40.8	18.4	40.8	24.9	72.6	2.5
29	750	33.3	11.1	55.6	40.2	56.7	3.1

TABLE E-14

Tar and Char Distribution - Highvale Coal

Run	Temp.(°C)	TAR DISTRIBUTION MECL2	ACET	G.WOOL	CHAR DISTRIBUTION BED	F.PAPER	REACT.
20	550	32.0	20.4	47.6	16.0	81.9	2.1
21	600	29.1	27.0	43.9	11.9	86.5	1.6
22	650	23.9	23.0	53.1	9.9	86.4	3.7
23	700	37.8	21.6	40.5	8.5	87.6	3.9
24	750	39.7	12.7	47.6	7.6	87.9	4.5